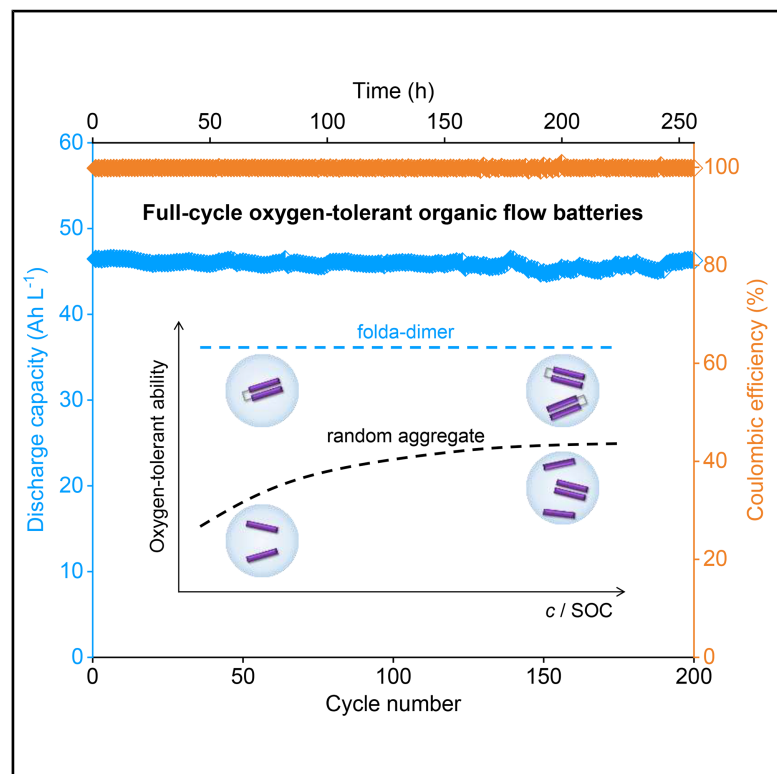


Full-cycle oxygen-tolerant organic flow batteries

Graphical abstract



Authors

Yufeng Liu, Kai Wan, Zhipeng Xiang, ..., Yi-Chun Lu, Shang-Da Jiang, Zhenxing Liang

Correspondence

huangmb@scut.edu.cn (M.H.),
yichunlu@mae.cuhk.edu.hk (Y.-C.L.),
zliang@scut.edu.cn (Z.L.)

In brief

This work presents a paradigm design for constructing a full-cycle oxygen-tolerant aqueous organic redox flow battery (AORFB). The folda-dimer structure enables the viologen negolyte with a concentration-independent oxygen-tolerant ability, providing high coulombic efficiency and superior cycling stability for AORFB operated under air.

Highlights

- Folda-dimer design enables concentration-independent oxygen-tolerant behavior
- Kinetic stability mechanism based on electronic coupling regulation is proposed
- Organic flow battery achieves full-cycle air tolerance and superior cycling stability



Article

Full-cycle oxygen-tolerant organic flow batteries

Yufeng Liu,¹ Kai Wan,¹ Zhipeng Xiang,^{1,5} Zhiyong Fu,^{1,6} Yuan Li,² Mingbao Huang,^{1,*} Yi-Chun Lu,^{3,*} Shang-Da Jiang,⁴ and Zhenxing Liang^{1,7,*}

¹Guangdong Provincial Key Laboratory of Fuel Cell Technology, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China

²Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510641, China

³Electrochemical Energy and Interfaces Laboratory, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong, Hong Kong SAR, China

⁴Spin-X Institute, School of Chemistry and Chemical Engineering, State Key Laboratory of Luminescent Materials and Devices, Guangdong-Hong Kong-Macao Joint Laboratory of Optoelectronic and Magnetic Functional Materials, South China University of Technology, Guangzhou 511442, China

⁵Institute for Sustainable Transformation, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

⁶Beijing Laboratory of New Energy Storage Technology, Beijing 102206, China

⁷Lead contact

*Correspondence: huangmb@scut.edu.cn (M.H.), yichunlu@mae.cuhk.edu.hk (Y.-C.L.), zliang@scut.edu.cn (Z.L.)

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CONTEXT & SCALE Aqueous organic redox flow batteries (AORFBs) are promising for grid-scale energy storage due to their high safety and sustainability. However, the oxygen sensitivity of reduced-state negolytes remains a critical limitation for ambient operation. This study presents a molecular design strategy that enables full-cycle oxygen tolerance via intramolecular folda-dimer formation. The folded conformation kinetically suppresses electron transfer to oxygen by reducing electronic coupling and uniquely imparts concentration-independent stability. By establishing a general kinetic framework for oxygen stabilization, this work paves the way for the development of air-stable organic electrolytes and will promote the practical deployment of AORFBs.

SUMMARY

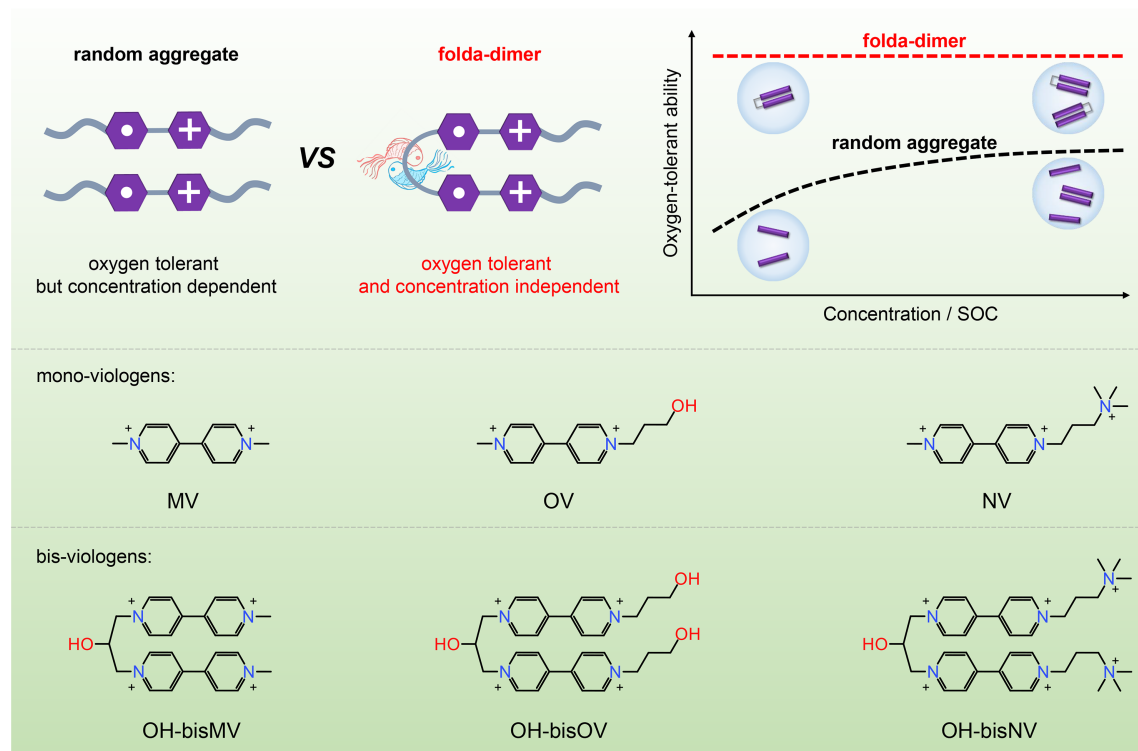
Aqueous organic redox flow batteries (AORFBs) are promising for safe and sustainable long-duration energy storage but suffer from the oxygen sensitivity of reduced-state negolyte species, which limits coulombic efficiency and cycling stability. Here, we develop a kinetic strategy to achieve full-cycle oxygen tolerance through the construction of folda-dimer. The folded conformation weakens the electronic coupling between the reduced-state molecule and oxygen, lowering the observed rate constant by two orders of magnitude compared with monomeric analogues. Moreover, this folded structure endows the system with concentration-independent characteristics, yielding full-cycle oxygen tolerance. As demonstrated, the AORFB with the bis-viologen negolyte shows a high capacity of 46.5 Ah L⁻¹, high coulombic efficiency of 99.9%, and superior cyclability (capacity retention rate of 99.96% per day in the configuration with 30% excess posolyte and 99.46% per day in the charge-balanced configuration) under air. This study establishes a kinetic stabilization paradigm for developing oxygen-tolerant electroactive organics of AORFBs.

INTRODUCTION

Aqueous flow batteries have been regarded as a safe and long-duration energy storage technology for the grid stabilization.^{1–3} Among these, the aqueous organic redox flow battery (AORFB) has attracted ever-growing attention due to the structural tunability and earth-abundant nature of electroactive organics.⁴ Electroactive molecules including quinone,^{5,6} aromatic heterocycle,^{7,8} viologen,^{9–12} and TEMPO^{13,14} have shown comparable

performance to the commercial all-vanadium system. However, the AORFB usually requires an inert atmosphere (e.g., Ar-filled glovebox) for its stable operation.¹⁵ The underlying reason lies in the pronounced oxygen sensitivity of reduced-state species in the negolyte, which triggers the capacity imbalance between the negolyte and posolyte, thereby compromising coulombic efficiency (CE) and driving rapid capacity fade.¹⁶ Thermodynamically, the reduced-state species can spontaneously react with oxygen, due to its lower redox potential (e.g., methyl viologen





Scheme 1. Schematic diagram of full-cycle oxygen-tolerant ability and design of bis-viologens with concentration-independent nature

[MV]; see [synthesis](#),¹⁷ -0.45 V versus standard hydrogen electrode [SHE]) than that of the oxygen reduction reaction. Kinetically, it has an extremely high reaction rate constant ($k > 10^7$ $\text{M}^{-1} \text{s}^{-1}$) of the reduced-state species with oxygen.^{18,19} The capacity fade caused by the oxygen attack would be very serious at a timescale of the battery's operation. Therefore, it is urgent to develop oxygen-tolerant negolytes to meet practical applications.

Elevating the thermodynamic potential of electroactive molecules is known to improve the oxygen tolerance,^{20–22} for example, grafting the strong electron-withdrawing group on viologen positively shifted its potential to 0.13 V, thus obtaining the oxygen-tolerant radical.²⁰ However, this strategy inevitably sacrifices the cell voltage, which is not ideal for the AORFB's applications. The kinetic strategy for improving the oxygen tolerance of negolyte seems to be a feasible approach.²¹ A host-guest assembly strategy could enhance the oxygen tolerance of the negolyte via steric hindrance.^{23,24} The β -cyclodextrin or cucurbit[8]uril as the host established a complex with the reduced-state viologen, which can block the oxygen attack. This strategy, however, faces inherent limitations from the host's low solubility (<0.5 M) and elevated viscosity, precluding the high-concentration battery operation. Beyond the steric hindrance, the π - π interaction-governed molecular aggregation can also enhance the stability of the reduced-state viologen.^{25,26} It is found that the aggregation phenomenon is highly dependent on the electrolyte's concentration, rendering a better air stability of flow battery with a concentrated electrolyte.²⁵ Such an intermolecular aggregation mode yields a typical concentration-dependent oxygen

tolerance (Scheme 1). Notably, the flow battery inevitably needs to go through a low state of charge (SOC), viz. low concentration of the reduced-state species, during the charge and discharge processes. Therefore, how to ensure the full-cycle (0%–100% SOC) air stability remains a great challenge.

Here, we report a kinetic stabilization strategy enabling the full-cycle air stability of negolyte through designing a concentration-independent folda-dimer architecture. In the supramolecular chemistry field, the confined conformation can be precisely manipulated by either host-guest assembly or covalent linkage.^{27,28} The latter approach enables the concentration-independent nature originating from the intramolecular interaction rather than intermolecular association.²⁸

Guided by this principle, we engineered three viologen derivatives (bis-viologens: 1-(2-hydroxy-3-{1'-methyl-[4,4'-bipyridine]-1,1'-diium-1-yl}propyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium dibromide dichloride [OH-bisMV]; 1-(2-hydroxy-3-{1'-(3-hydroxypropyl)-[4,4'-bipyridine]-1,1'-diium-1-yl}propyl)-1'-(3-hydroxypropyl)-[4,4'-bipyridine]-1,1'-diium tetrabromide [OH-bisOV]; and 1-(2-hydroxy-3-{1'-methyl-[4,4'-bipyridine]-1,1'-diium-1-yl}propyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium dibromide dichloride [OH-bisNV]; see [synthesis](#); Scheme 1; Scheme S1; Figures S1–S4) featuring isopropanol-bridged bipyridinium units. Parallel synthesis of mono-viologens (MV, 1-(3-hydroxypropyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium dichloride [OV], and 1'-methyl-1-[3-(trimethylazaniumyl)propyl]-[4,4'-bipyridine]-1,1'-diium trichloride [NV]; see [synthesis](#); Schemes S2 and S3; Figures S5–S8) with identical substituents provides essential comparative controls. Experimental and theoretical analyses

converge to demonstrate that reduced-state bis-viologens adopt a concentration-independent folded conformation, which is stabilized by a pancake bond.²⁹ We found that the formation of folda-dimers alters the orientation between oxygen and reduced-state bis-viologen molecule. Such a change weakens their electronic coupling and consequently slows the electron transfer, reducing the observed rate constant by two orders of magnitude compared with monomeric analogues. As a demonstration, a flow battery fed with 1.0 M OH-bisOV electrolyte (corresponding to 2.0 M electron concentration) ran for 10.7 days under air, offering a high CE (99.9%) and remarkable cycling stability (capacity retention rate of 99.998% per cycle or 99.96% per day) at 40 mA cm⁻².

RESULTS

Electrochemical behaviors of bis-viologens

The redox behavior of mono-viologens and bis-viologens was studied by cyclic voltammetry (CV). The CVs (Figure S9) of MV, OV, NV, OH-bisMV, OH-bisOV, and OH-bisNV show reversible redox peaks with a formal potential of -0.65, -0.63, -0.59, -0.52, -0.51, and -0.48 V, respectively. The peak separations (ΔE_p) of MV, OV, and NV are identified as 59, 60, and 59 mV, respectively; and bis-viologens are identified as 34, 39, and 37 mV, respectively, suggesting that the bis-viologens undergo a two-electron transfer process.³⁰ This process is depicted in Figure S10, where the redox potential (E_2) of the second-electron reduction step is more positive than that of the first-electron reduction step (E_1), namely potential inversion.³⁰ The underlying reason for the potential inversion is investigated by thermodynamic analysis (Table S1). The results show that the two-electron reduced bis-viologen (OH-bisVi²⁽⁺⁾) is more stable than the one-electron reduced bis-viologen (OH-bisVi³⁺), thereby yielding a one-step two-electron process.

The diffusion coefficient (D) was derived from the steady-state current collected on a gold disk microelectrode (Figure S11). The linear sweeping voltammograms (LSVs; Figure S12) show that OH-bisMV, OH-bisOV, and OH-bisNV yield a limiting current of 5.3, 4.4, and 3.9 nA, from which the D is calculated as 4.2×10^{-6} , 3.4×10^{-6} , and 3.1×10^{-6} cm² s⁻¹, respectively. These values are slightly lower than those of corresponding mono-viologens. It is understandable that the D value decreases with the increase of molecular mass. The electron transfer rate constant (k^0) is estimated by electrochemical digital simulation (Figure S13). All the redox processes of OH-bisMV, OH-bisOV, and OH-bisNV show very high k^0 values (>0.3 cm s⁻¹). Such a high reversibility correlates with a small recombination energy of the bis-viologens (Table S2). The physicochemical properties of bis-viologens are summarized in Table S3. Taken together, the as-prepared bis-viologens have a high aqueous solubility, high reversibility, and decent redox potential, making them promising negolytes for AORFBs.

Determination of folda-dimer for reduced-state bis-viologens

To investigate the structure of reduced-state bis-viologens, sodium dithionite (Na₂S₂O₄) was used as the reducing agent to generate the two-electron-reduced species OH-bisVi²⁽⁺⁾ (namely,

OH-bisMV²⁽⁺⁾, OH-bisOV²⁽⁺⁾, and OH-bisNV²⁽⁺⁾) in buffer solutions (Figure 1A). These reduced products were characterized by the ultraviolet-visible-near infrared (UV-vis-NIR) and electron paramagnetic resonance (EPR) spectroscopy. The normalized UV-vis-NIR spectra of reduced-state bis-viologens at different concentrations are shown in Figures 1B and S14. It is found that reduced-state bis-viologens have the same absorption bands around 533 and 837 nm, and the normalized curves at different concentrations (from 1 to 250 μ M) almost overlap. These two absorption bands correspond to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) + 2 and HOMO-LUMO leaps (Figure S15) of the viologen-radical dimer.³¹ Importantly, the absorption bands do not show any dependence on the solution concentration, implying that the reduced-state bis-viologens form the folda-dimer.³² In contrast, the absorption band is not seen at 800–900 nm for the reduced-state mono-viologen solution when its concentration is below 100 μ M (Figures 1C and S14). An absorption band emerges around 870 nm for MV⁺ and OV⁺ with an increase in concentration to 500 μ M, while there is still no absorption band for NV²⁺. It does highlight that the intermolecular aggregation of reduced-state mono-viologens is highly dependent on the concentration. To probe the effect of linker length on folda-structure for bis-viologen, we engineered bis-viologen (1'-methyl-1-(2-{1'-methyl-[4,4'-bipyridine]-1,1'-diium-1-yl}ethyl)-[4,4'-bipyridine]-1,1'-diium dibromide dichloride [Et-bisMV]; see synthesis; Scheme S4; Figures S16 and S17) with a shorter linker. The reduced-state Et-bisMV²⁽⁺⁾ shows intermolecular aggregation, which is similar to the reduced-state mono-viologens (Figure S18), rather than their folded form. It is inferred that the shorter length of linker can hinder the formation of folda-structure in space.

Such folded behavior of bis-viologens was investigated by EPR. As shown in Figures 1D and S19, the EPR signal intensities of the reduced-state bis-viologens are significantly weaker than those of reduced-state mono-viologens (Figures 1E and S19) with the same concentration at 298 K. Moreover, as the temperature increases from 298 to 358 K, the EPR signals of the three reduced-state bis-viologens are gradually enhanced, while it remains almost unchanged for the reduced-state mono-viologens. First, the weaker EPR signals of OH-bisMV²⁽⁺⁾, OH-bisOV²⁽⁺⁾, and OH-bisNV²⁽⁺⁾ suggest that they form a pancake bond, resulting in the formation of diamagnetic dimers.³³ Second, these diamagnetic species are converted to the paramagnetic species with increasing temperature.³² The above results confirm the formation of folda-dimer with a pancake bond.

The folda-structure of the reduced-state bis-viologens was further revealed by the density functional theory (DFT) calculations. The electron energy and free energy of three conformations (including singlet folda-structure, triplet folda-structure, and triplet unfolda-structure) were calculated at a M06-2X/def2tzvp level.^{34,35} It is found that the singlet folda-structure has the lowest free energy (Figures 1F and S20; Table S4). In addition, the simulated electronic spectrum of the singlet conformation is highly similar to the experimental one, while the result of triplet conformation is different from them (Figure 1G). These results fully suggest that such a folda-structure tends to be at singlet state, which agrees well with the results of the above UV-vis-NIR and EPR (*vide supra*).

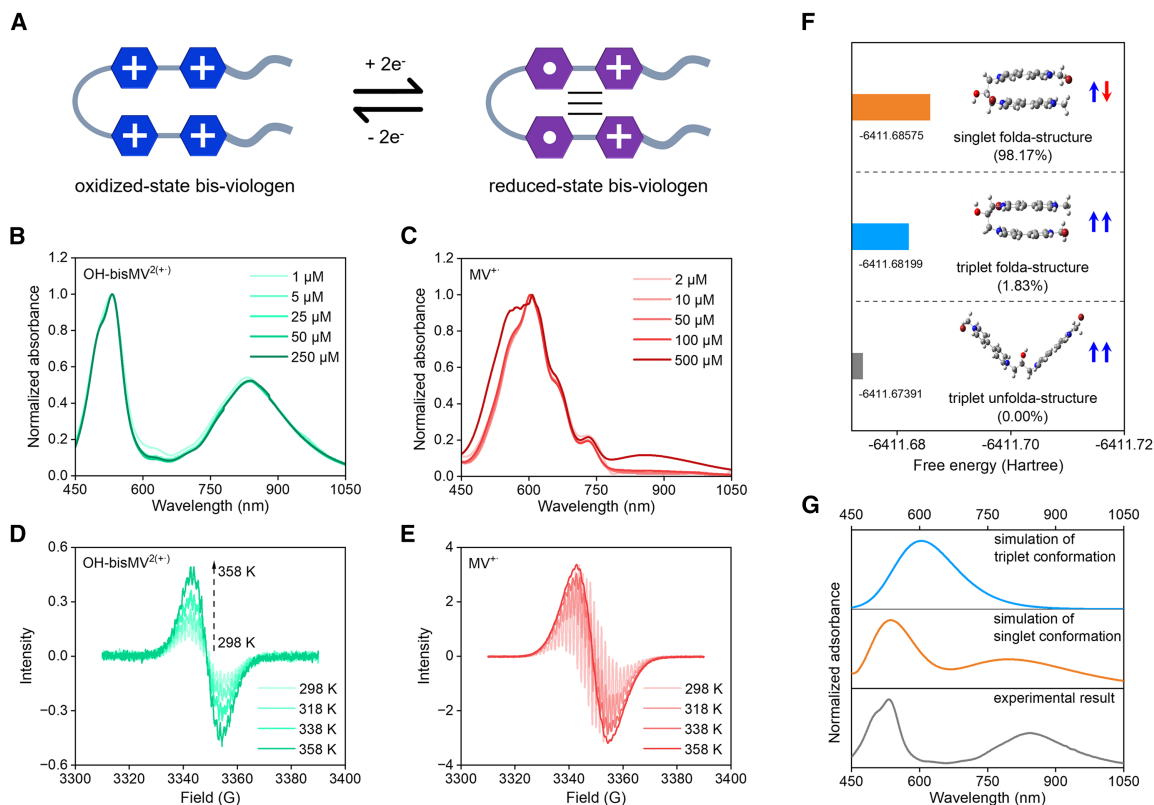


Figure 1. Spectral characterizations and calculations of reduced-state bis-viologens

(A) Scheme of reduction of bis-viologens.

(B and C) UV-vis-NIR spectra of (B) OH-bisMV²⁽⁺⁾ and (C) MV⁺ at different concentrations.

(D and E) EPR spectra of (D) 2.0 mM OH-bisMV²⁽⁺⁾ and (E) 4.0 mM MV⁺ at different temperatures.

(F) Calculated free energy and Boltzmann distribution (298 K) of three conformations of OH-bisMV²⁽⁺⁾ at M06-2X/def2tzvp level.

(G) Experimental and simulated electronic spectra at PBE1PBE/6-31g(d, p) level.

Mechanism of oxygen tolerance for reduced-state bis-viologens

The reaction between the reduced-state bis-viologens and O₂ was studied by Marcus theory and the equation expression is as follows.

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \frac{|H_{\text{DA}}|^2}{\sqrt{4\pi\lambda k_{\text{B}}T}} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}}T}\right) \quad (\text{Equation 1})$$

$$\Delta G_{\text{RC}}^{\ddagger} = \frac{(\lambda + \Delta G^0)^2}{4\lambda} \quad (\text{Equation 2})$$

where k_{ET} is the rate constant for electron transfer, $|H_{\text{DA}}|$ is the electronic coupling between the initial and final state, λ is the reorganization energy, and ΔG^0 is the Gibbs free energy change for the electron transfer reaction.

It is seen from Equation 2, both λ and ΔG^0 affect the activation barrier free energy ($\Delta G_{\text{RC}}^{\ddagger}$). We thus calculated the λ and ΔG^0 of the electron transfer reaction between the reduced-state molecules (MV⁺, OV⁺, NV²⁺, OH-bisMV²⁽⁺⁾, OH-bisOV²⁽⁺⁾, and OH-bisNV²⁽⁺⁾) and O₂ at the M06-2X/def2tzvp level. The results are summarized in Table S5. It is found that the ΔG^0 is −0.35,

−0.21, −0.20, −0.16, −0.12, and −0.14 eV, respectively; and the λ is 3.53, 3.51, 3.57, 3.25, 3.20, and 3.28 eV, respectively. Finally, the $\Delta G_{\text{RC}}^{\ddagger}$ is further obtained as 0.72, 0.77, 0.79, 0.73, 0.74, and 0.75 eV, respectively. These results indicate that there is a very small difference in $\Delta G_{\text{RC}}^{\ddagger}$ for the reduced-state viologen molecules.

Therefore, we further investigated the $|H_{\text{DA}}|$ through the 2-state Generalized Mulliken-Hush (GMH) model.^{36,37} As the orientation and distance between the reactants can usually affect the $|H_{\text{DA}}|$, we accordingly performed the cluster configuration (O₂ + reduced-state mono/bis-viologens) searches by the Molclus program,³⁸ which are summarized in Tables S6–S11. It is seen that the O₂ molecule tends to lie on the bipyridine torus for the reduced-state mono-viologens (Figure 2A; Tables S6–S8), while it tends to bind on the side of reduced-state bis-viologens (Figure 2A; Tables S9–S11). The difference results from their different minimum point sites of van der Waals potential on the surface³⁹ (Figures S21 and S22), further affecting the dispersion-interaction sites.

The reactivity is determined by the overlap of molecular orbitals. Based on the optimized cluster configurations, the overlap integral is calculated (Figure S23). The overlap integrals between the reduced-state bis-viologens and O₂ are much less than

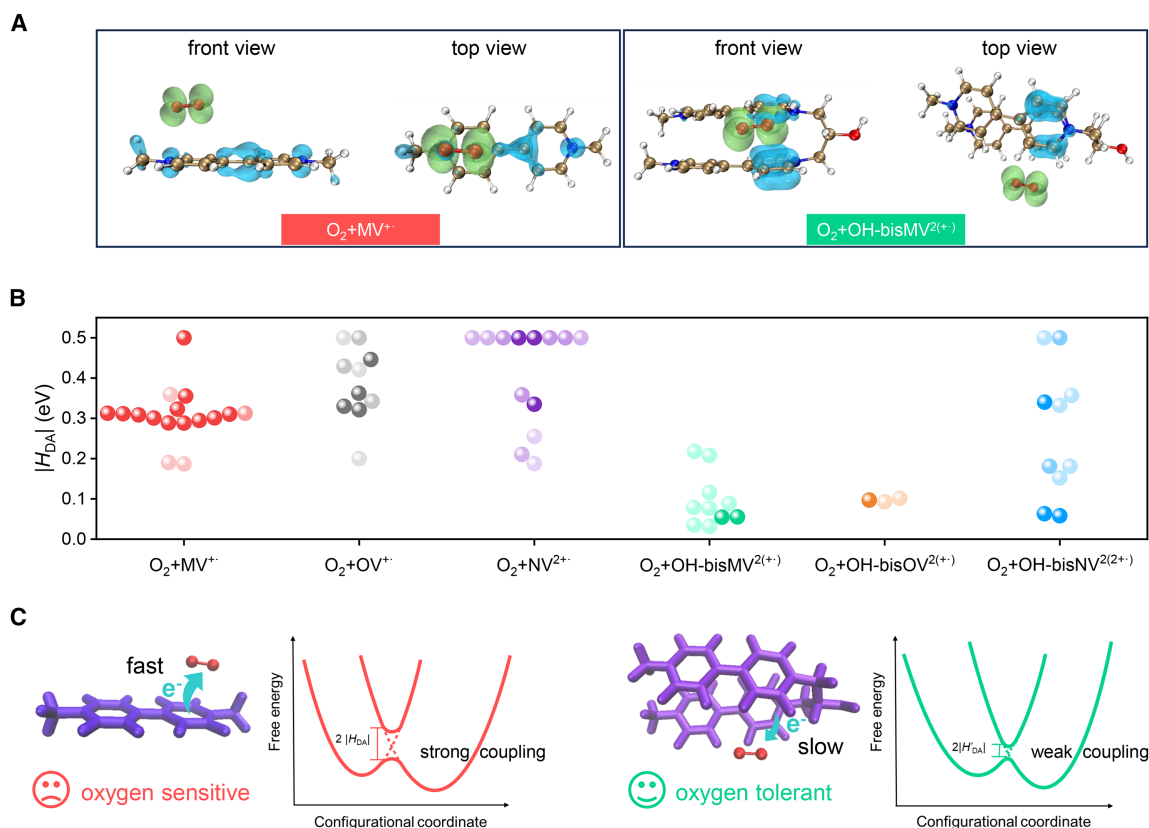


Figure 2. Electronic coupling analysis

(A) Schematic diagrams of the optimized $O_2 + MV^{+}$ configuration and the $O_2 + OH\text{-bis}MV^{2(+)}$ configuration, and the isosurface of electron (green)-hole (blue) distribution.

(B) $|H_{DA}|$ calculated by the GMH method (note, here the value of $|H_{DA}| \geq 0.5$ is set to 0.5 and dark color represents high Boltzmann ratio).

(C) Schematic diagram of kinetic mechanism of oxygen tolerance based on electronic coupling.

those between the reduced-state mono-viologen and O_2 , suggesting a small $|H_{DA}|$.⁴⁰ Further, the $|H_{DA}|$ is calculated by the 2-state GMH method, which is also summarized in Tables S6–S11. As shown in Figure 2B, the $|H_{DA}|$ of O_2 +reduced-state mono-viologen configurations is mainly distributed above 0.3 eV, while those of $O_2 + OH\text{-bis}MV^{2(+)}$ and $O_2 + OH\text{-bis}OV^{2(+)}$ configurations are below 0.1 eV. It is acknowledged that the smaller $|H_{DA}|$ value means a lower k_{ET} , thereby yielding a higher O_2 -tolerant ability (Figure 2C). It is noteworthy that the $|H_{DA}|$ of $O_2 + OH\text{-bis}NV^{2(2+)}$ configurations has a wide distribution ranging from 0.06 to 1.22 eV. The high value may be due to the electrostatic repulsion effect of positively charged quaternary ammonium groups at the terminal,⁴¹ resulting in a larger singlet-triplet energy gap (ΔE_{S-T} , Table S12). It is speculated that such an effect is negative to maintain a robust folda-dimer.

Oxygen tolerance of bis-viologen negolytes upon exposure to air

The observed pseudo-first-order rate constant (k_{obs}) between the reduced-state viologen molecules and O_2 was evaluated by the electrochemical method using carbon paper as the working electrode (Figure S24).⁴² As shown in Figure S25, all

CVs show a reversible diffusion-control behavior under an Ar atmosphere. The reduction current increases when O_2 is introduced into the system, due to the existence of O_2 reduction processes mediated by the reduced-state viologens. The deviation of the CV from the classical S-shape is caused by the low-concentration O_2 in aqueous solutions (Figures S25 and S26), in which case the k_{obs} can be extracted by the foot-of-the-wave analysis (FOWA).⁴³ The k_{obs} of MV^{+} , OV^{+} , NV^{2+} , $OH\text{-bis}MV^{2(+)}$, $OH\text{-bis}OV^{2(+)}$, and $OH\text{-bis}NV^{2(2+)}$ reacting with O_2 is determined to be 2.0×10^5 , 1.1×10^5 , 1.6×10^5 , 2.1×10^3 , 3.0×10^3 , and 1.2×10^4 s⁻¹, respectively (Figure 3A). As expected, the bis-viologen system shows a smaller k_{obs} than does mono-viologen. Among them, the k_{obs} values of $OH\text{-bis}MV^{2(+)}$ with O_2 and $OH\text{-bis}OV^{2(+)}$ with O_2 are two orders of magnitude smaller than that of mono-viologen with O_2 . As such, the $OH\text{-bis}MV^{2(+)}$ and $OH\text{-bis}OV^{2(+)}$ have a better oxygen-tolerant ability, which is consistent with above $|H_{DA}|$ results. Also, the $Et\text{-bis}MV^{2(+)}$ shows a high oxygen sensitivity ($k_{obs} = 1.2 \times 10^5$ s⁻¹, Figure S27), which is similar to the reduced-state mono-viologens, further suggesting that the enhanced oxygen tolerance indeed originates from the folda-dimer effect.

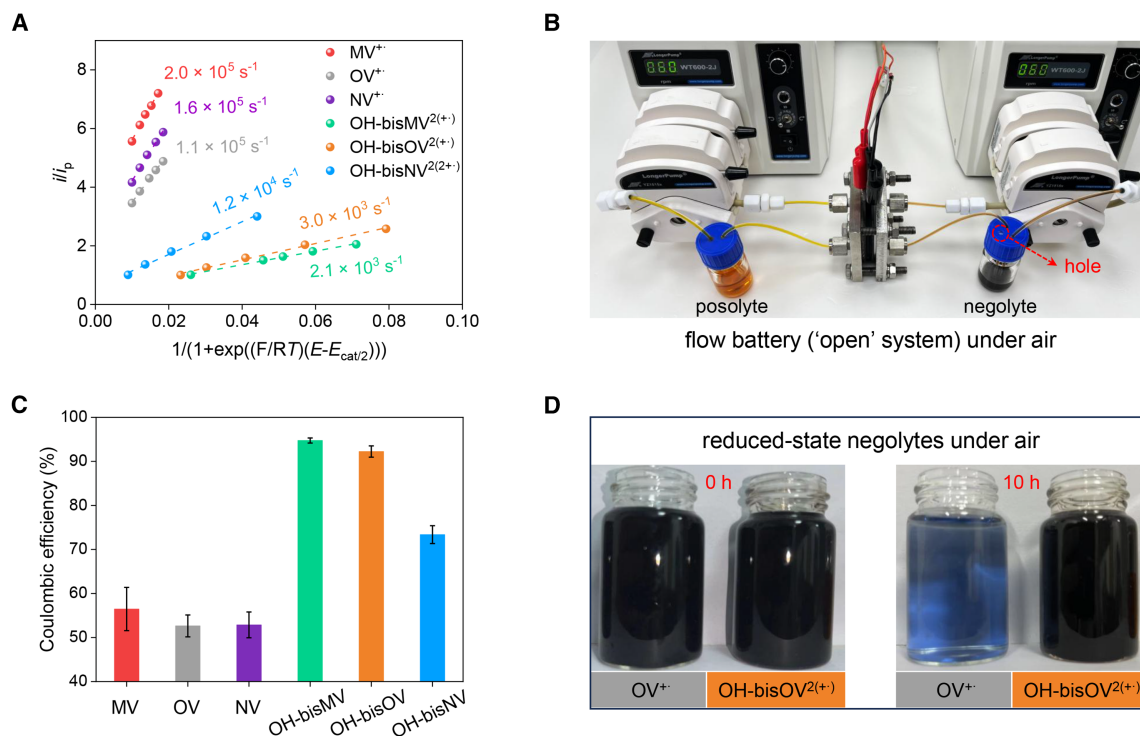


Figure 3. Oxygen tolerance of bis-viologen negolytes exposure to air

(A) The k_{obs} between O_2 and reduced-state viologens derived from FOWA.

(B) Photo of the flow battery (open system) device under air.

(C) CEs of the flow battery (open system) under air with either 0.10 M bis-viologen or 0.20 M mono-viologen as the negolyte and 0.20 M FcNCl as the posolyte. (Data are represented as mean $\pm$ SEM).

(D) Photos of the 10.0 mM $OV^{+•}$ and 5.0 mM $OH-bisOV^{2(+)}$ negolytes exposed to air over different times.

The O_2 tolerance of the bis-viologen electrolytes was further verified by testing a flow battery in an air atmosphere. Here, a flow battery fed with either 0.10 M bis-viologen or 0.20 M mono-viologen as the negolyte is operated to ensure the same theoretical capacity. To rigorously evaluate the air stability of the negolyte, it is fully exposed to air through a 3-mm diameter hole ("open" system, Figure 3B). Quantitative analysis of the CE during charge-discharge cycling (Figure 3C) reveals the marked performance differences: MV (56% $\pm$ 5%), OV (53% $\pm$ 2%), NV (53% $\pm$ 3%), OH-bisMV (95% $\pm$ 1%), OH-bisOV (92% $\pm$ 1%), and OH-bisNV (73% $\pm$ 2%). These results show that the bis-viologen electrolytes demonstrate a substantially improved air stability compared with the mono-viologen electrolytes. We also observed a similar behavior in additional molecular system (1-[3-(trimethylazaniumyl)propyl]-4-[5-(1-[3-[4-(5-[1-[3-(trimethylazaniumyl)propyl]pyridin-1-ium-4-yl]thiophen-2-yl)pyridin-1-ium-1-yl]propyl]pyridin-1-ium-4-yl]thiophen-2-yl)pyridin-1-ium hexabromide [bisATBPY]; see synthesis; Scheme S5; Figures S28–S31), where the fold-dimer exhibits superior CE relative to its monomeric counterpart.

In addition, it is observed that the O_2 tolerance of OH-bisNV is inferior to the other two bis-viologens, which complies with the mechanistic analyses (*vide supra*). It is worth noting that at this concentration (0.20 M), even though it can form the intermolec-

ular aggregation for the reduced-state mono-viologens,³¹ yet they do not show sufficient tolerance against O_2 . This is probably due to the low dimerization constant of the reduced-state mono-viologens (313–420 M^{-1} , Figure S32), and the equilibrium releases a considerable amount of monomeric form for reacting with O_2 . Especially, the flow battery inevitably needs to go through a low SOC, viz. low concentration of the reduced-state species, during the charge and discharge processes, which makes the situation worse.

Based on above understanding and bis-viologen's solubility, the OH-bisOV was selected as a target for following study. First, we investigated the effect of SOC on oxygen tolerance of negolyte. Comparative analysis in Figure S33 demonstrates the marked SOC-dependent oxygen sensitivity in mono-viologen (OV): CEs of 68% $\pm$ 1% at 90%–100% SOC versus 48% $\pm$ 3% at 0%–10% SOC. In contrast, the bis-viologen (OH-bisOV) maintains SOC-independent air stability (CEs of 90% $\pm$ 1% at 0%–10% SOC versus 91% $\pm$ 1% at 90%–100% SOC). It is highlighted that the fold-dimer of the reduced-state bis-viologens is independent of the concentration, which yields a superior concentration-independent air stability. Further, the reduced-state negolyte solutions (10.0 mL 10.0 mM $OV^{+•}$ and 10.0 mL 5.0 mM $OH-bisOV^{2(+)}$) contained in two transparent bottles are directly exposed to air to intuitively observe the degeneration process. As shown in Figures 3D and S34, the dark purple

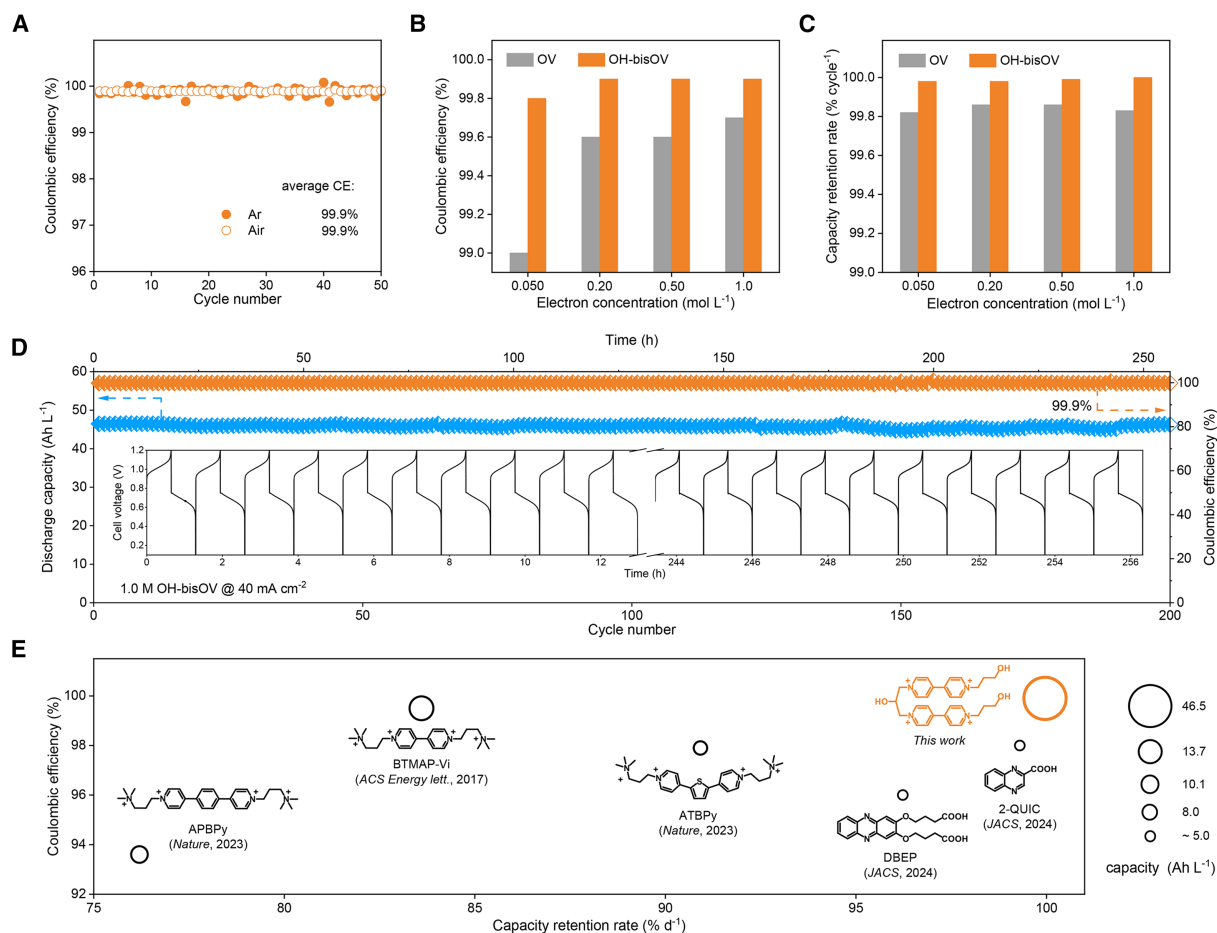


Figure 4. Flow battery (closed system) performance under air

- (A) CEs of the flow battery fed with 0.25 M OH-bisOV at 40 mA cm⁻² under air or Ar atmosphere.
 (B) CEs of flow battery fed with different concentration electrolytes (electron concentration: 0.050, 0.20, 0.50, and 1.0 M) under air.
 (C) Corresponding capacity retention rates of flow battery at different concentrations.
 (D) Cycling performance of the flow battery fed with 1.0 M OH-bisOV (2.0 M electron concentration) at 40 mA cm⁻² under air.
 (E) Summary of the CE, demonstrated capacity and retention rate of representative negolyte systems cycled under air.^{25,41,44,45}

OV⁺ solution turns light blue after 10 h, while the OH-bisOV²⁽⁺⁾ solution maintains its dark purple color.

Flow battery performance under air

We performed full-flow battery tests (“closed” system) in air to compare the stability with other reported organic negolytes. First, systems employing 0.50 M OV or 0.25 M OH-bisOV negolyte were cycled either inside or outside Ar-filled glovebox. As shown in Figure 4A, the flow battery fed with 0.25 M OH-bisOV operated in ambient air achieves a high average CE of 99.9%—matching the glovebox-maintained counterpart. This demonstrates the feasibility of oxygen-tolerant operation in an air environment. In comparison, the flow battery fed with 0.50 M OV exhibits a high CE of 99.9% under Ar but decreases to 99.6% under air (Figure S35). It is noted that the CEs of both OV and OH-bisOV based flow batteries are significantly improved compared with the open system. This improvement arises from the isolation of air in the closed configuration,

which substantially suppresses the oxygen-induced side reactions.

We further systematically evaluated the concentration effect on oxygen tolerance by testing OV and OH-bisOV negolytes (electron concentrations, 0.050, 0.20, 0.50, and 1.0 M) under air. As shown in Figures 4B, 4C, and S36, all the OH-bisOV-based flow batteries demonstrate high CEs (99.8%, 99.9%, 99.9%, and 99.9%, respectively) and remarkable cycling stability (capacity retention rate of >99.98% per cycle) at different operating concentrations. In comparison, the OV-based flow batteries show inferior CEs (99.0%, 99.6%, 99.6%, and 99.7%, respectively) and poor cycling performance (capacity retention rate of <99.86% per cycle). These results emphasize the superior and concentration-independent oxygen tolerance of bis-viologen OH-bisOV negolyte, while the mono-viologen OV negolyte displays a typical concentration-dependent air stability. Notably, even at 1.0 M, the oxygen tolerance of OV negolyte is still insufficient, which is

understandable as the flow battery needs to go through a low SOC process (*vide supra*).

To evaluate the intrinsic electrochemical stability of the bis-viologen molecule, we performed long-term cycling test (Figure S37) on a symmetric battery employing 0.10 M OH-bisOV electrolyte. The system exhibits an exceptional cycling stability over ~12 days with a total capacity decay of 0.05% (about 0.004% per day)—the lowest decay rate among reported negolytes to date (Table S13), confirming the molecular stability. As a demonstration, we performed a flow battery operation with 1.0 M OH-bisOV electrolyte (2.0 M electron concentration) under air. As shown in Figure S38, the flow battery with a charge-balanced configuration (equal capacity between the posolyte and the negolyte) demonstrates a high CE of ~99.9%, indicating its high oxygen-tolerant capability. During the 100-cycle test, the flow battery shows a decent cycling stability, with a capacity retention rate of 99.971% per cycle (or 99.46% per day). To isolate the posolyte's contribution to capacity loss, we further tested a flow battery with 30% excess posolyte. It is seen from Figure 4D that the system achieves a high capacity of 46.5 Ah L⁻¹ at 40 mA cm⁻², high average CE of 99.9%, and capacity retention rate of 99.58% (99.998% per cycle, 99.96% per day) over 200 cycles (10.7 days). Post-cycling analysis of the OH-bisOV electrolyte by ¹H nuclear magnetic resonance (NMR) spectroscopy showed no obvious by-products (Figure S39), indicating its high chemical stability during battery operation. These performances establish bis-viologen's superior air stability compared with other representative systems (Figure 4E; Table S14), demonstrating its advantages in CE, capacity, and stability.

DISCUSSION

In summary, we develop a kinetic strategy to improve the oxygen tolerance of organic electroactive molecules applied to negolyte, without sacrificing the redox potential. The folded conformation plays a key role in stabilizing the reduced-state bis-viologen negolyte. First, the formation of a folda-dimer can reduce the $|H_{DA}|$, and thus effectively improves the intrinsic tolerance of reduced-state bis-viologen against oxygen. Second, the concentration-independent folda-dimer ensures a robust oxygen tolerance of negolyte at different concentrations or SOC conditions. Finally, the flow battery achieves a full-cycle air stability, delivering a high capacity of 46.5 Ah L⁻¹, high CE (~99.9%), and remarkable cycling performance (capacity retention rate of 99.998% per cycle or 99.96% per day) under air. This work demonstrates an unprecedented air-stable AORFB and provides a key descriptor to design oxygen-tolerant electrolyte in the future, which paves the way for the practical application of AORFBs.

METHODS

Chemicals

All of the reagents were commercially available and used without further purification. 4,4'-bipyridine (98%, Shanghai Aladdin Bio-Chem Technology, China), 2,5-di(pyridin-4-yl)thiophene (98%, Shanghai Haohong Biomedical Technology, China), 1,3-dibromo-2-propanol (95%, Shanghai Macklin Biochemical, China),

1,2-dibromoethane (98%, Anhui Zesheng Technology, China), 1,3-dibromopropane (98%, Anhui Zesheng Technology, China), chloroacetic acid (98%, Shanghai Macklin Biochemical), N-(3-bromopropyl)-N,N,N-trimethylammonium bromide (97%, Ark Pharm, USA), 3-bromo-1-propanol (97%, Shanghai Aladdin Bio-Chem Technology, China), iodomethane (99.5%, TCI [Shanghai] Development, China), KCl (analytical pure, Guangzhou Chemical Reagent Factory, China), KOH (analytical pure, Guangzhou Chemical Reagent Factory, China), dimethyl formamide (DMF, analytical pure, Chinasun Specialty Products, China), acetonitrile (ACN, analytical pure, Shanghai Lingfeng Chemical Reagent, China), and acetone (analytical pure, Guangzhou Chemical Reagent Factory, China) were used as received.

Synthesis

OH-bisBpy

In a 250 mL two-necked flask, 4,4'-bipyridine (21.5 g, 137.8 mmol) was added into 100 mL ACN. 1,3-Dibromo-2-propanol (5.0 g, 22.9 mmol) was added into a constant pressure funnel containing 20 mL ACN. Then, the solution containing 1,3-dibromo-2-propanol was slowly added into the two-necked flask and subsequently reacted for 48 h at 85°C. After cooling to room temperature, the off-white precipitate was collected by filtration. The precipitate was then added into 200 mL ACN and sonicated for 1 h to remove unreacted feedstock, followed by filtration and vacuum drying to collect the pure product (9.75 g, 18.4 mmol, and 80% yield). The ¹H NMR spectrum of 1-(3-[[4,4'-bipyridin]-1-ium-1-yl]-2-hydroxypropyl)-[4,4'-bipyridin]-1-ium dibromide [OH-bisBpy] is shown in Figure S1.

OH-bisMV

As-prepared OH-bisBpy (2.0 g, 3.8 mmol), chloroacetic acid (0.9 g, 9.5 mmol), and 100 mL DMF were added into a 250 mL round-bottomed flask. The mixture was stirred at 150°C for 24 h. After cooling to room temperature, the brown precipitate was collected by filtration and washed with 20 mL ACN. Finally, the pure product of OH-bisMV (2.3 g, 3.6 mmol, and 95% yield) was obtained by vacuum drying for 12 h. The ¹H NMR and ¹³C NMR spectra of OH-bisMV are shown in Figure S2.

OH-bisOV

As-prepared OH-bisBpy (2.0 g, 3.8 mmol), 3-bromo-1-propanol (3.5 g, 25 mmol), and 100 mL DMF were added into a 250 mL round-bottomed flask. The mixture was stirred at 100°C for 48 h. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with 30 mL ACN. Finally, the pure product of OH-bisOV (2.2 g, 2.7 mmol, and 71% yield) was obtained by vacuum drying for 12 h. The ¹H NMR and ¹³C NMR spectra of OH-bisOV are shown in Figure S3.

OH-bisNV

As-prepared OH-bisBpy (2.0 g, 3.8 mmol), N-(3-bromopropyl)-N,N,N-trimethylammonium bromide (2.6 g, 10 mmol), and 100 mL DMF were added into a 250 mL round-bottomed flask. The mixture was stirred at 120°C for 24 h. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with 20 mL ACN. Finally, the pure product of OH-bisNV (3.6 g, 3.4 mmol, and 90% yield) was obtained by vacuum drying for 12 h. The ¹H NMR and ¹³C NMR spectra of OH-bisNV are shown in Figure S4.

MV

The 1,1'-dimethyl-[4,4'-bipyridine]-1,1'-diium dichloride (MV) is synthesized according to the literature method¹⁷ (Scheme S2), and the ¹H NMR spectrum of MV is shown in Figure S5.

Me-Bpy

In a 250 mL round-bottom flask, 4,4'-bipyridine (5.0 g, 32 mmol) was added into 100 mL acetone. Then methyl iodide (4.3 g, 30 mmol) was added into the flask and reacted for 12 h at room temperature. The precipitate was filtered and washed with 30 mL acetone, and the yellow 1-methyl-[4,4'-bipyridin]-1-ium iodide (Me-Bpy) powder (7.5 g, 25 mmol, and 83% yield) was obtained after vacuum drying. The ¹H NMR spectrum of Me-Bpy is shown in Figure S6.

OV

As-prepared Me-Bpy (5.0 g, 17 mmol), 3-bromo-1-propanol (6.5 g, 30 mmol), and 100 mL DMF were added into a 250 mL round-bottomed flask. The mixture was stirred at 85°C for 48 h. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with 50 mL ACN. The precipitate was dried and then the ion exchange was carried out. Finally, the pure product of 1-(3-hydroxypropyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium dichloride (OV) (3.3 g, 11 mmol, and 65% yield) was obtained and the ¹H NMR spectrum is shown in Figure S7.

NV

As-prepared Me-Bpy (3.0 g, 10 mmol), N-(3-bromopropyl)-N,N,N-trimethylammonium bromide (3.1 g, 12 mmol) and 100 mL DMF were added into a 250 mL round-bottomed flask. The mixture was stirred at 120°C for 24 h. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with 30 mL ACN. The precipitate was dried and then the ion exchange was carried out. Finally, the pure product of 1'-methyl-1-[3-(trimethylazaniumyl)propyl]-[4,4'-bipyridine]-1,1'-diium trichloride (NV) (3.0 g, 8 mmol, and 80% yield) was obtained and the ¹H NMR spectrum is shown in Figure S8.

Et-bisBpy

In a 250 mL two-necked flask, 4,4'-bipyridine (21.5 g, 137.6 mmol) was added into 100 mL ACN. 1,2-dibromoethane (4.3 g, 22.9 mmol) was added into a constant pressure funnel containing 20 mL ACN. Then, the solution containing 1,2-dibromoethane was slowly added into the two-necked flask and subsequently reacted for 48 h at 80°C. After cooling to room temperature, the off-white precipitate was collected by filtration. Finally, the pure product (10.1 g, 88% yield) was collected by washing with 20 mL ACN and vacuum drying. The ¹H NMR spectrum of 1-(2-[[4,4'-bipyridin]-1-ium-1-yl]ethyl)-[4,4'-bipyridin]-1-ium dibromide (Et-bisBpy) is shown in Figure S16.

Et-bisMV

As-prepared Et-bisBpy (5.0 g, 10 mmol), chloroacetic acid (2.36 g, 25 mmol), and 250 mL DMF were added into a 500 mL round-bottomed flask. The mixture was stirred at 150°C for 24 h. After cooling to room temperature, the brown precipitate was collected by filtration and washed with 50 mL ACN. Finally, the pure product of Et-bisMV (5.59 g, 93% yield) was obtained by vacuum drying for 12 h. The ¹H NMR and ¹³C NMR spectra of Et-bisMV are shown in Figure S17.

bisTBPpy

In a 100 mL two-necked flask, 2,5-di(pyridin-4-yl)thiophene (10 g, 42 mmol) was added into 30 mL DMF. 1,3-dibromopro-

pane (2.1 g, 10.5 mmol) was added into a constant pressure funnel containing 10 mL DMF. Then, the solution containing 1,3-dibromopropane was slowly added into the two-necked flask and subsequently reacted for 48 h at 80°C. After cooling to room temperature, the yellow precipitate was collected by filtration. Finally, the pure product (6.05 g, 85% yield) was collected by washing with 20 mL ACN and vacuum drying. The ¹H NMR spectrum of 4-[5-(pyridin-4-yl)thiophen-2-yl]-1-(3-{4-[5-(pyridin-4-yl)thiophen-2-yl]pyridin-1-ium-1-yl}propyl)pyridin-1-ium dibromide (bisTBPpy) is shown in Figure S28.

bisATBPpy

As-prepared bisTBPpy (2.0 g, 2.9 mmol), N-(3-bromopropyl)-N,N,N-trimethylammonium bromide (2.1 g, 8 mmol), and 50 mL DMF were added into a 100 mL round-bottomed flask. The mixture was stirred at 120°C for 48 h. After cooling to room temperature, the yellow precipitate was collected by filtration and washed with 20 mL ACN. Finally, the pure product of bisATBPpy (3.1 g, 2.6 mmol, and 89% yield) was obtained by vacuum drying for 12 h. The ¹H NMR and ¹³C NMR spectra of bisATBPpy are shown in Figure S29.

Physicochemical characterizations

¹H NMR spectra were collected on an AVANCE III HD 600 MHz (Bruker, Germany). UV-vis-NIR spectra were collected on a Hitachi UV-5700 (Japan) spectrometer equipped with an optional integrating sphere. EPR tests were conducted on a Bruker ELEXSYS-II E500 CW-EPR (Germany) spectrometer. The EPR parameters for all experiments are as follows: modulation frequency = 100 kHz, modulation amplitude = 1.0 G, conversion time = 20.00 ms, sweep time = 60.00 s, microwave attenuation = 20 dB, and microwave power = 2.000 mW. The Q values for MV⁺, OV⁺, NV²⁺, OH-bisMV^{2(+·)}, OH-bisOV^{2(+·)}, and OH-bisNV^{2(2+·)} are 2,200, 1,900, 1,800, 2,900, 2,700, and 2,400, respectively.

For the structural characterization, reduced-state viologen solutions were prepared by chemical reduction. For the oxygen-tolerant test, the reduced-state viologen solutions were prepared by electrolysis in order to avoid interference from other species.

Solubility tests

A general UV-vis method was employed to determine the aqueous solubility of viologens. Specifically, a small amount of viologen powder was accurately weighed using an analytical balance and dissolved in ultrapure water. The solution was transferred into a 5 mL volumetric flask and then diluted to the mark to obtain the viologen solution with known concentration. This solution was further diluted with ultrapure water to prepare at least five viologen solutions with varying concentrations. The UV-vis spectra of these diluted solutions were recorded, and the absorbance at the maximum absorption wavelength (~266 nm) was measured. A standard calibration curve was constructed by plotting absorbance (≤1.0) versus concentration.

To prepare the saturated solution, the viologen powder was added to 1 mL ultrapure water until no more could dissolve. The supernatant was collected and filtered through a 0.22-μm syringe filter to remove any undissolved particles, yielding a saturated solution. This saturated solution was diluted to an appropriate extent so that its absorbance fell within the linear

range of the standard curve. Finally, the aqueous solubility of viologens was calculated based on the dilution factor and the standard curve. All measurements were conducted at room temperature.

Electrochemical tests

A CHI730E (Shanghai, China) electrochemical workstation was used to collect the cyclic voltammogram (CV) with a standard three-electrode setup, including glassy carbon (diameter of 3.0 mm) working electrode, Ag/AgCl reference electrode, and platinum counter electrode. LSV was used to collect the limiting current of electroactive component by using the gold disk microelectrode with a scan rate of 50 mV s⁻¹. The D can thus be obtained according to a steady-state current equation as follows:

$$i_{ss} = 4nFDC_0r_0 \quad (\text{Equation 3})$$

where i_{ss} is the steady-state current (A), n is the electron transfer number, F is the Faraday constant (= 96485 C mol⁻¹), D is the diffusion coefficient (cm² s⁻¹), C_0 is the bulk concentration of electroactive component, and r_0 is the radius of the microelectrode ($\approx 16.4 \mu\text{m}$).

The electron transfer rate constant was obtained through digital simulation on CHI 730E software. For mono-viologens, the single-electron electrochemical mechanism (E) is used for simulation; for bis-viologens, a continuous single-electron mechanism (EE) is employed for simulation. Some parameters including the thermodynamic potential, diffusion coefficient, electrode area (0.07068 cm²), and scan rate (1 V s⁻¹) are fixed during the simulation.

DFT calculations

All DFT calculations were performed by using Gaussian 09⁴⁶ program. The initial configurations were optimized at the M06-2X/def2svp level, including the empirical dispersion correction (GD3)^{47,48} and the implicit solvation model based on solute electron density (SMD). All optimized structures were checked by harmonic vibrational frequencies to ensure that they were on the minima of potential energy surface (imaginary frequency = 0). The electron energies were calculated at the M06-2X/def2tzvp level based on the optimized configurations. The van der Waals potential of the optimized structure was analyzed by Multiwfn⁴⁹ and drawn by the VMD⁵⁰ package.

Cluster configuration search

The 500 initial cluster configurations of reduced-state viologen molecule and oxygen were generated by using Molclus program and optimized at GFN-xTB level using xtb.⁵¹ The optimized structures were further optimized at M06-2X/def2svp level by Gaussian 09 program after clustering.

Electronic coupling calculations

The electric coupling matrix elements ($|H_{DA}|$) of reduced-state viologen and oxygen were calculated using the 2-state GMH model.³⁶ A time-dependent DFT (TDDFT) method was used to calculate the excited state of the optimized configuration. The first 40 excited states of optimized configuration were calculated at CAM-B3LYP/6-31G(d, p) using Gaussian 09 program.

In the 2-state GMH model, $|H_{DA}|$ between states 1 and 2 was calculated using the following equation:

$$|H_{DA}| = \frac{|\mu_{12}|\Delta E_{12}}{\sqrt{(\mu_{11} - \mu_{22})^2 + 4(\mu_{12})^2}} \quad (\text{Equation 4})$$

ΔE_{12} is the vertical excitation energy, μ_{12} is the transition dipole moment, and μ_{11} and μ_{22} are the ground state and excited state dipole moments respectively.

The charge transfer was calculated by interfragment charge transfer (IFCT) method at Mulliken level using Multiwfn program. The electron-hole distance (ΔR)⁵² of the excited state was also calculated by using Multiwfn program. In many cases, ΔR is almost equal to the center of mass distance (r_{com}). In our application, the charge transfer state was taken as the charge transfer amount greater than 0.8 and the $\Delta R > 0.8r_{com}$. For configurations with multiple charge transfer states, the excited state with the highest oscillator intensity is used for $|H_{DA}|$ calculation.

Observed reaction rate constant (k_{obs}) tests

For homogeneous catalytic reaction, the CV curve is of a classical S-shape when there is no side-phenomenon to perturb the reaction. In viologen-mediated oxygen reduction reaction, the CV curve will deviate from the classical S-shape due to the low solubility of oxygen in water, in which case the k_{obs} between reduced-state viologen and oxygen can be extracted by FOWA developed by Savéant and coworkers.⁴³ The FOWA is encapsulated by Equation 5, in which i is the current at given potential E under the catalytic conditions (O_2) and i_p is the non-catalytic current of the viologen derivations, v is the scan rate (1 V s⁻¹), $E_{redox} = E_{cat/2}$,⁵³ $k_{obs} = k'_{obs}/C_{O_2}$, and the concentration of dissolved oxygen is approximated as 1.25 mM.

$$\frac{i}{i_p} = \frac{2.24\sqrt{\frac{RT}{Fv}}\sqrt{2k'_{obs}}}{1 + \exp\left[\frac{F}{RT}(E - E_{redox})\right]} \quad (\text{Equation 5})$$

During the test, the carbon paper (size, 2 mm $\times$ 2 mm) was used as the working electrode, and the sweep rate was set to 1 V s⁻¹.

Flow battery tests

A laboratory-scale flow battery was assembled as follows. Graphite felt electrodes (3 cm $\times$ 3 cm in size, 5-mm thick) were placed beside the titanium current collectors. A Selemin DSVN anion-exchange membrane (AGC Selemin) was used as the separator. The electrolytes were circulated through the cell by a peristaltic pump (Longer BT1002J) at a flow rate of 60 mL min⁻¹. The battery test was performed on a Neware BTS 3000 battery testing system. The flow battery was tested by a galvanostatic charge-discharge method under room temperature.

For flow battery (open system) tests under air atmosphere the following conditions were used: (A) 6.0 mL negolyte containing 0.20 M mono-viologens (MV, OV, or NV) or 0.10 M bis-viologen (OH-bisMV, OH-bisOV, or OH-bisNV) in 2.0 M KCl_{aq} and 20.0 mL posolyte containing 0.20 M FcNCl⁵⁴ in 2.0 M KCl_{aq}

were used. The negolyte was exposed to air through a 3-mm diameter hole. The flow batteries were operated at 20 mA cm⁻² with a 10 s rest duration. (B) 20.0 mL negolyte containing 0.025 M ATBPy or 0.0125 M bisATBPy in 2.0 M KCl_{aq} and 20.0 mL posolyte containing 0.025 M FcNCl in 2.0 M KCl_{aq} were used. The negolyte was exposed to air through a 3-mm diameter hole. The flow batteries were operated at 10 mA cm⁻² with a 10 s rest duration.

For flow battery (closed system) tests under air atmosphere: (A) 10.0 mL negolyte 0.025 M OH-bisOV or 0.050 M OV in 2.0 M KCl_{aq} and 11.0 mL posolyte 0.050 M FcNCl in 2.0 M KCl_{aq} were used. (B) 7.0 mL negolyte 0.10 M OH-bisOV or 0.20 M OV in 2.0 M KCl_{aq} and 16.0 mL posolyte 0.10 M FcNCl in 2.0 M KCl_{aq} were used. (C) 5.0 mL negolyte 0.25 M OH-bisOV or 0.50 M OV in 2.0 M KCl_{aq} and 27.0 mL posolyte 0.10 M FcNCl in 2.0 M KCl_{aq} were used. (D) 5.0 mL negolyte 0.50 M OH-bisOV or 1.0 M OV in 2.0 M KCl_{aq} and 55.0 mL posolyte 0.10 M FcNCl in 2.0 M KCl_{aq} were used. (E) 5.0 mL negolyte 1.0 M OH-bisOV in 1.0 M KCl_{aq} and 130.0 mL (or 100.0 mL) posolyte 0.10 M FcNCl in 2.0 M KCl_{aq} were used, and the flow batteries were operated at 40 mA cm⁻² with a 5 s rest duration. For the 1.0 M flow battery test, a potentiostatic discharge to 12 mA cm⁻² was set within the voltage cut-off 0.1–1.2 V.

Here, we define the closed system as the flow battery equipped with all components, and the open system specifically refers to the configuration drilled with an open hole on the reservoir lid. For the closed system, all electrolytes were purged with argon for 10 min prior to use to remove the dissolved oxygen. The flow battery was assembled and tested under ambient air without the use of an inert atmosphere.

For the symmetric flow battery test, 10 mL 0.10 M OH-bisOV was charged to a reduced state (100% SOC) as the non-capacity limiting site of the symmetric battery, and 5.0 mL 0.10 M OH-bisOV (0% SOC) as the capacity limiting site of the symmetric battery. The flow battery was operated at 40 mA cm⁻² with a 5 s rest duration. The symmetric flow battery test was performed under argon atmosphere.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Zhenxing Liang (zliang@scut.edu.cn).

Materials availability

The materials are available from the corresponding authors on reasonable request.

Data and code availability

The data shown in the plots and that support the findings of this study are available from the corresponding authors on reasonable request. The experimental results can be found in the [supplemental information](#).

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AUTHOR CONTRIBUTIONS

Y. Liu and M.H. conceived the idea and designed the experiments. M.H., Z.F., and Z.L. supervised the project. Y. Liu conducted the experiments and data analysis. K.W. and Z.X. conducted the electrochemical measurements. Y. Liu contributed to the DFT simulation. Z.F., Y. Li, and S.-D.J. contributed to the data analysis. Y. Liu, M.H., Y.-C.L., and Z.L. organized and wrote the manuscript. All authors contributed to the discussion and have given approval to the final version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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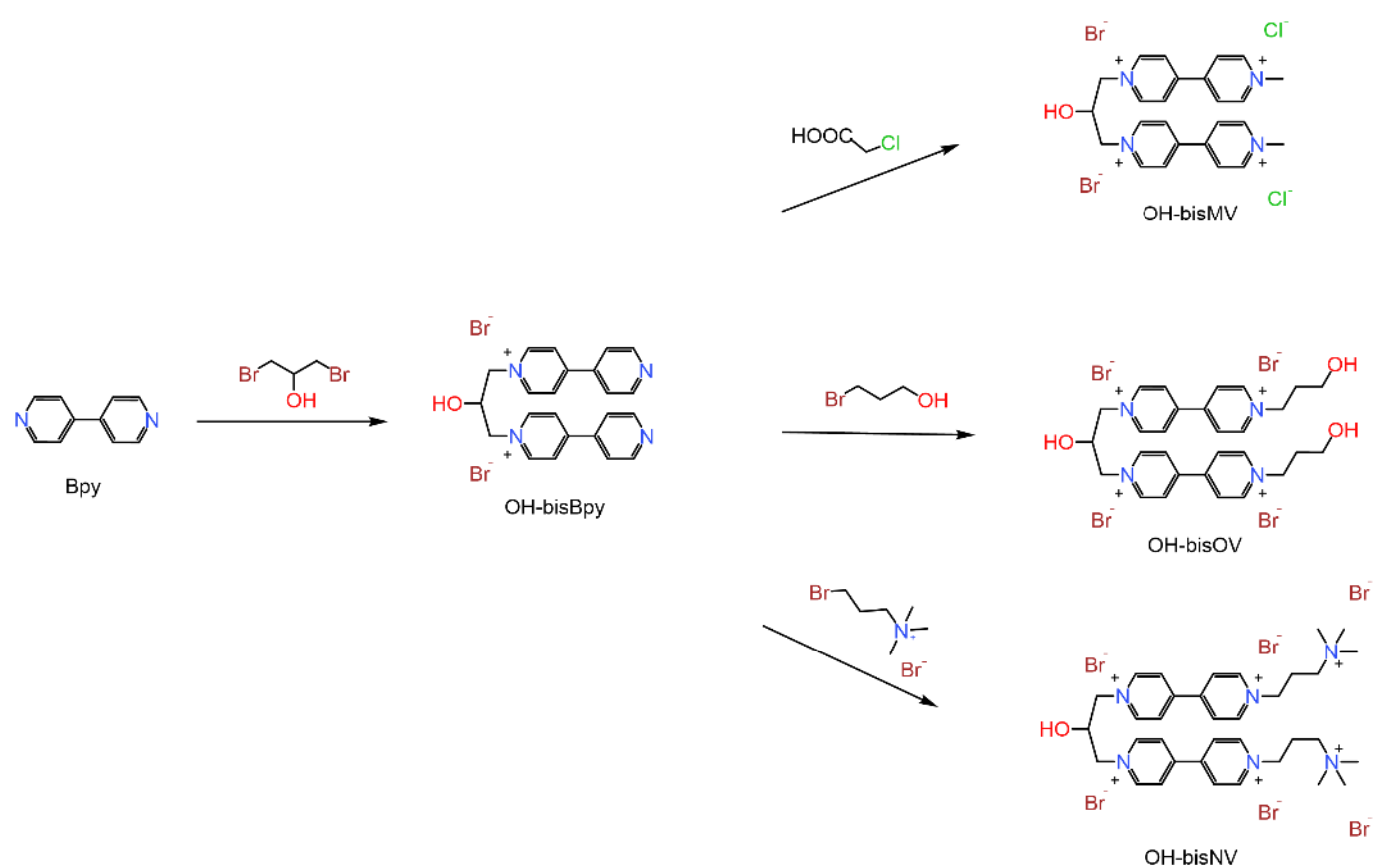
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Supplemental information

Full-cycle oxygen-tolerant organic flow batteries

Yufeng Liu, Kai Wan, Zhipeng Xiang, Zhiyong Fu, Yuan Li, Mingbao Huang, Yi-Chun Lu, Shang-Da Jiang, and Zhenxing Liang



Scheme S1. Synthesis protocol of bis-viologens.

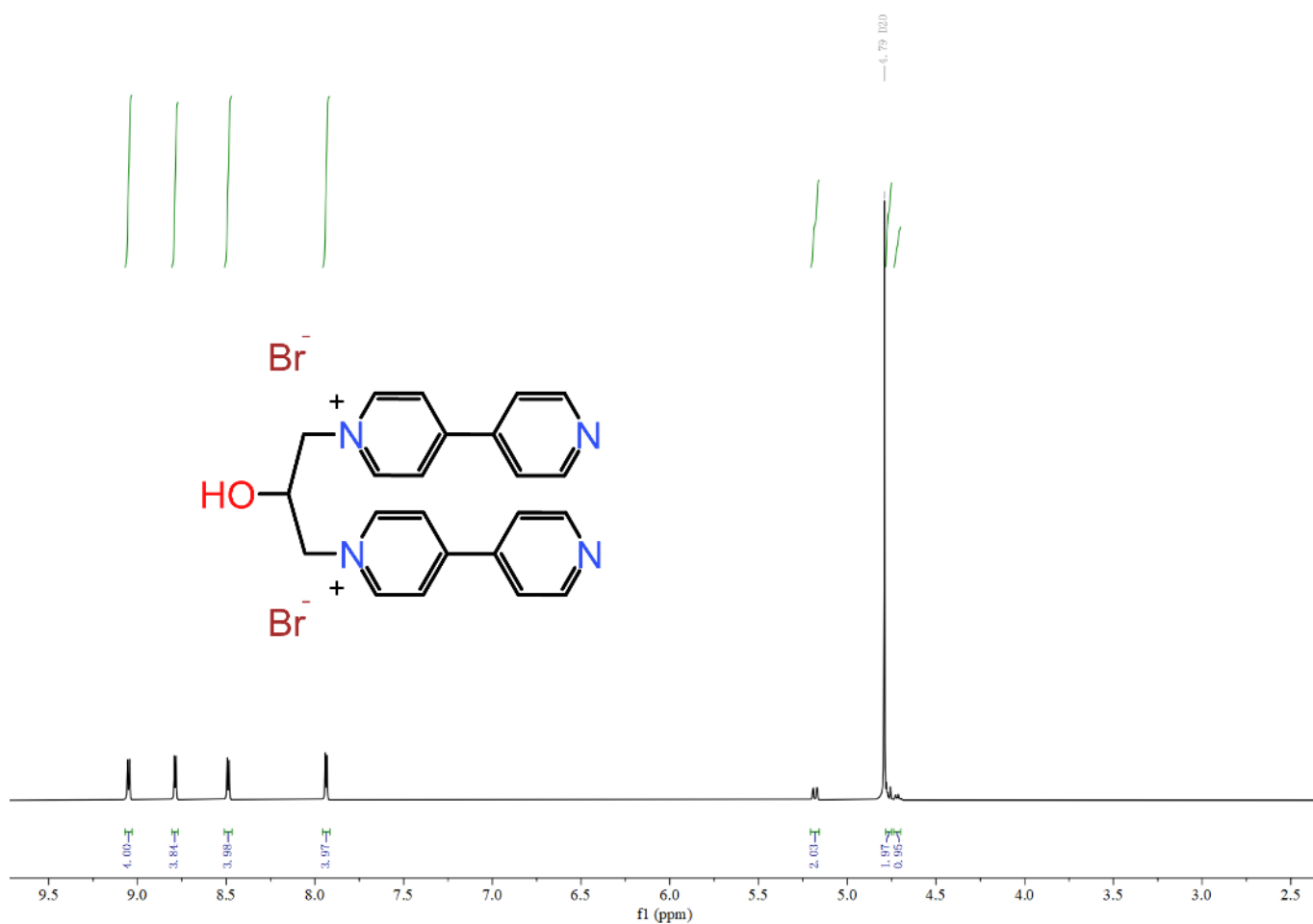
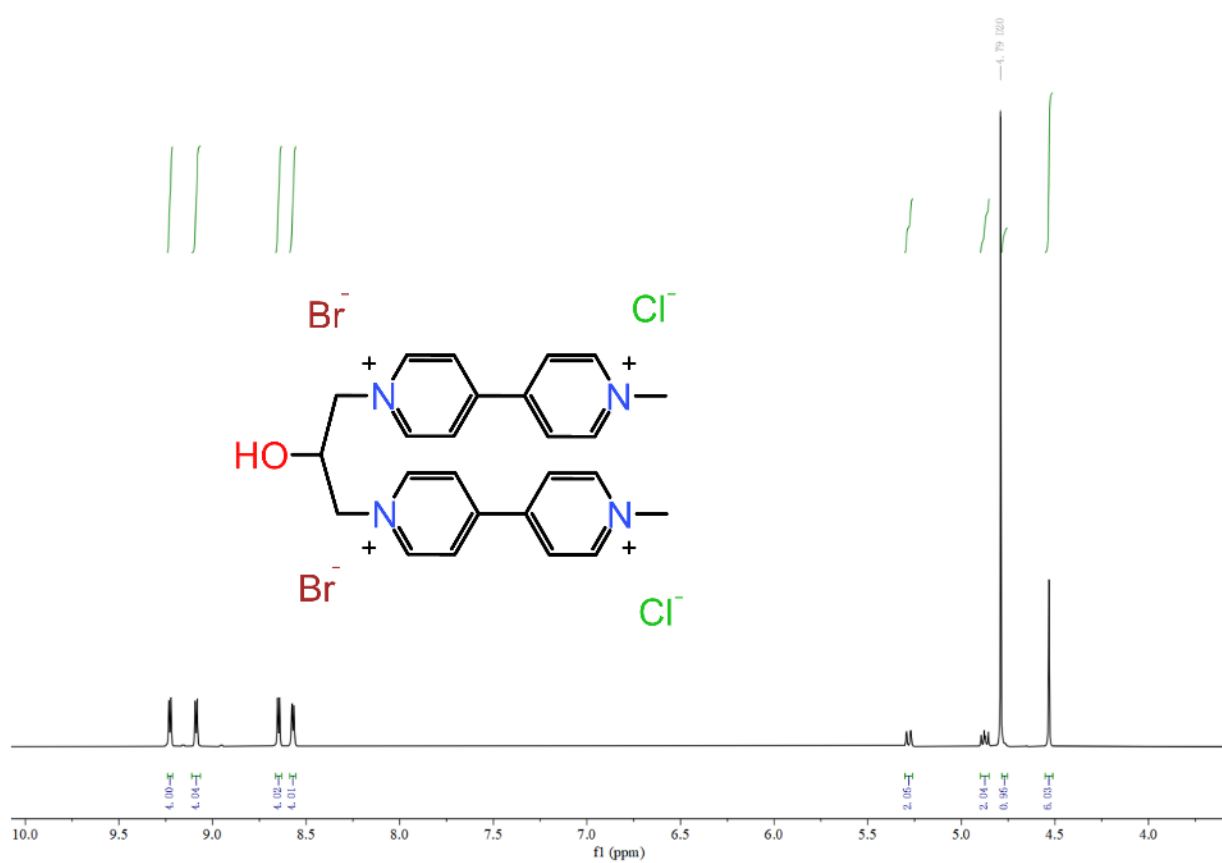


Figure S1. ^1H NMR spectrum of OH-bisBpy (D_2O).

A



B

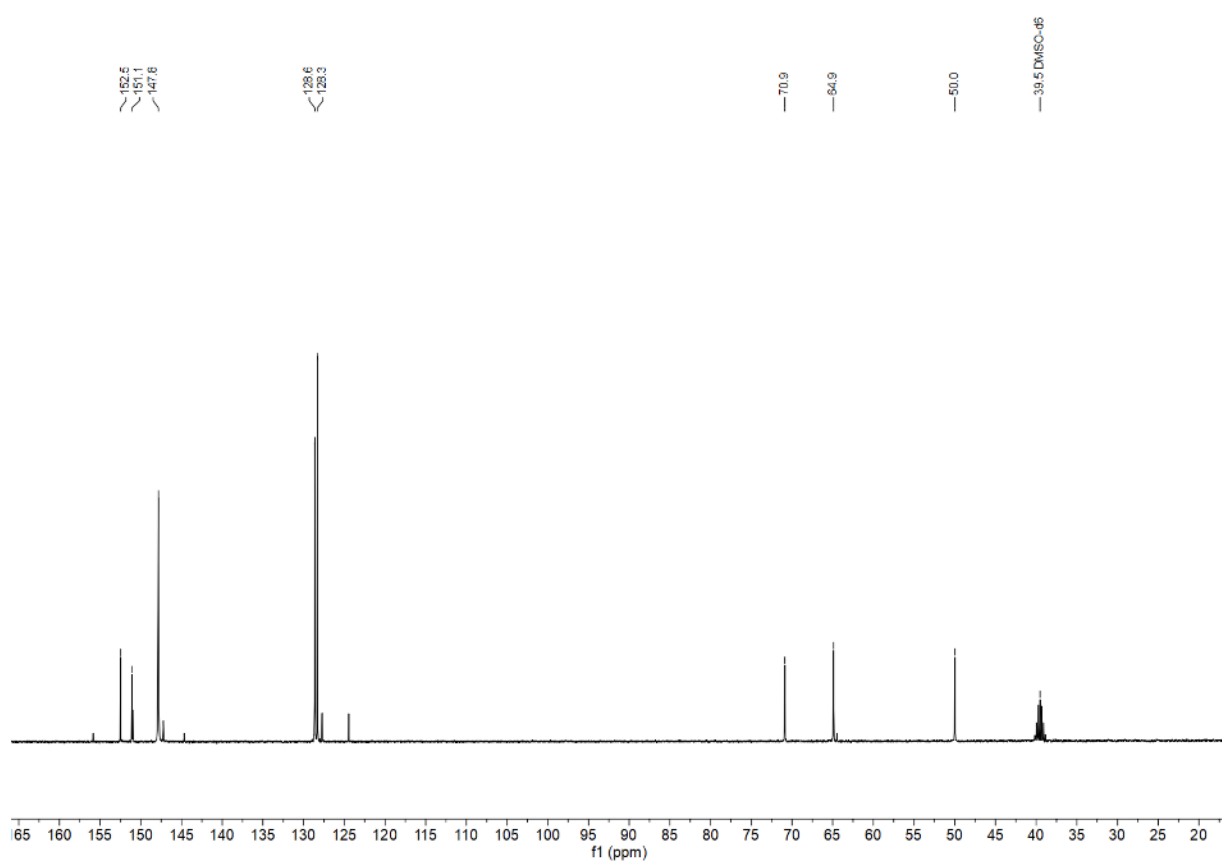
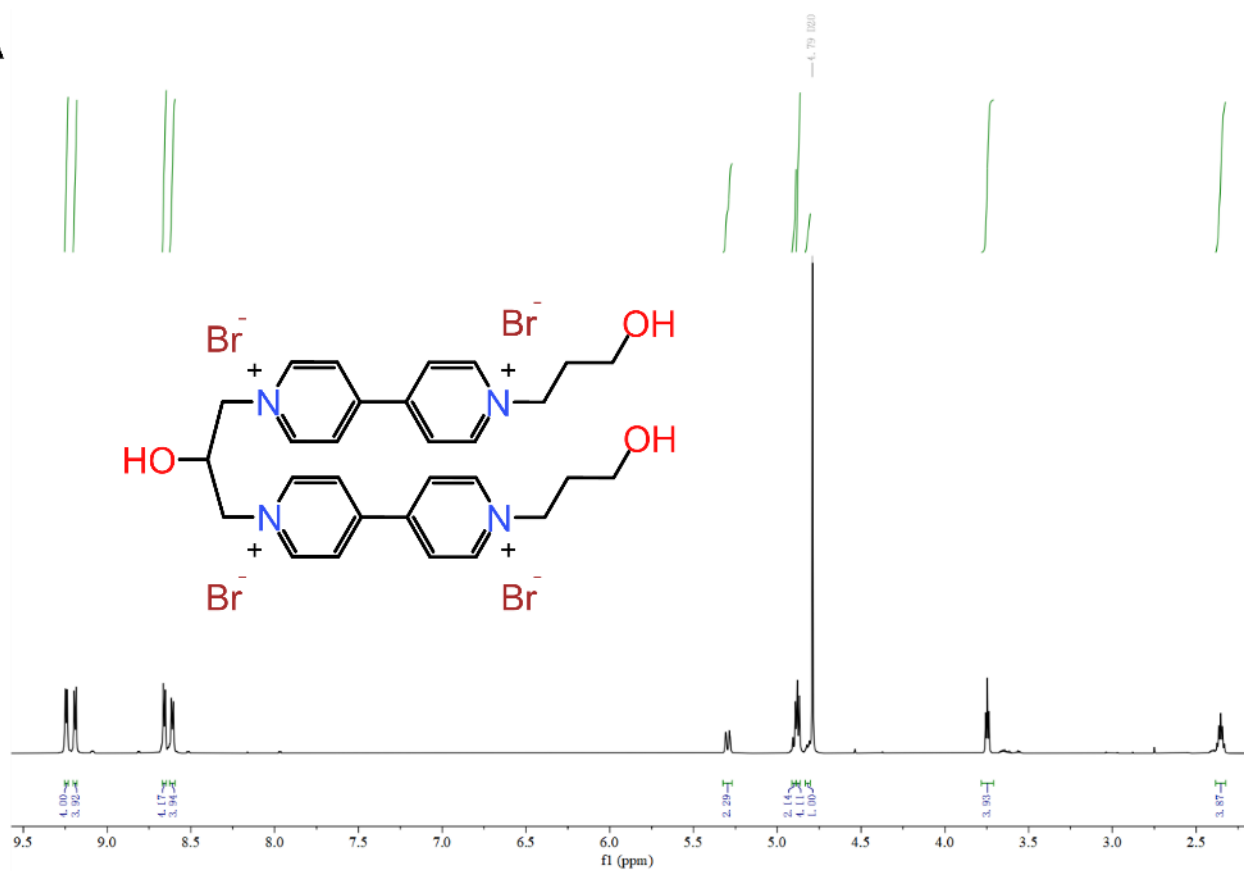


Figure S2. NMR spectra of OH-bisMV. (A) ¹H NMR (D₂O); (B) ¹³C NMR (D₂O with a drop of DMSO-*d*₆).

A

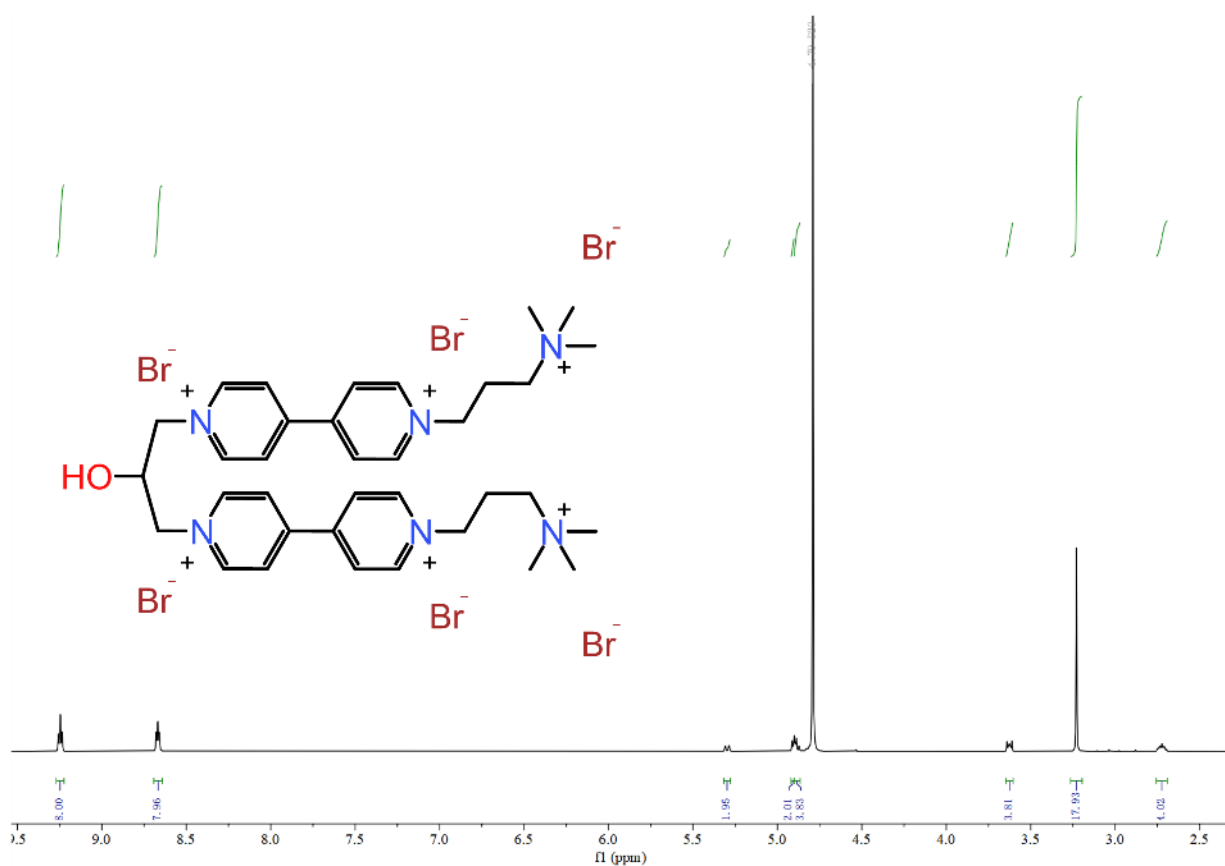
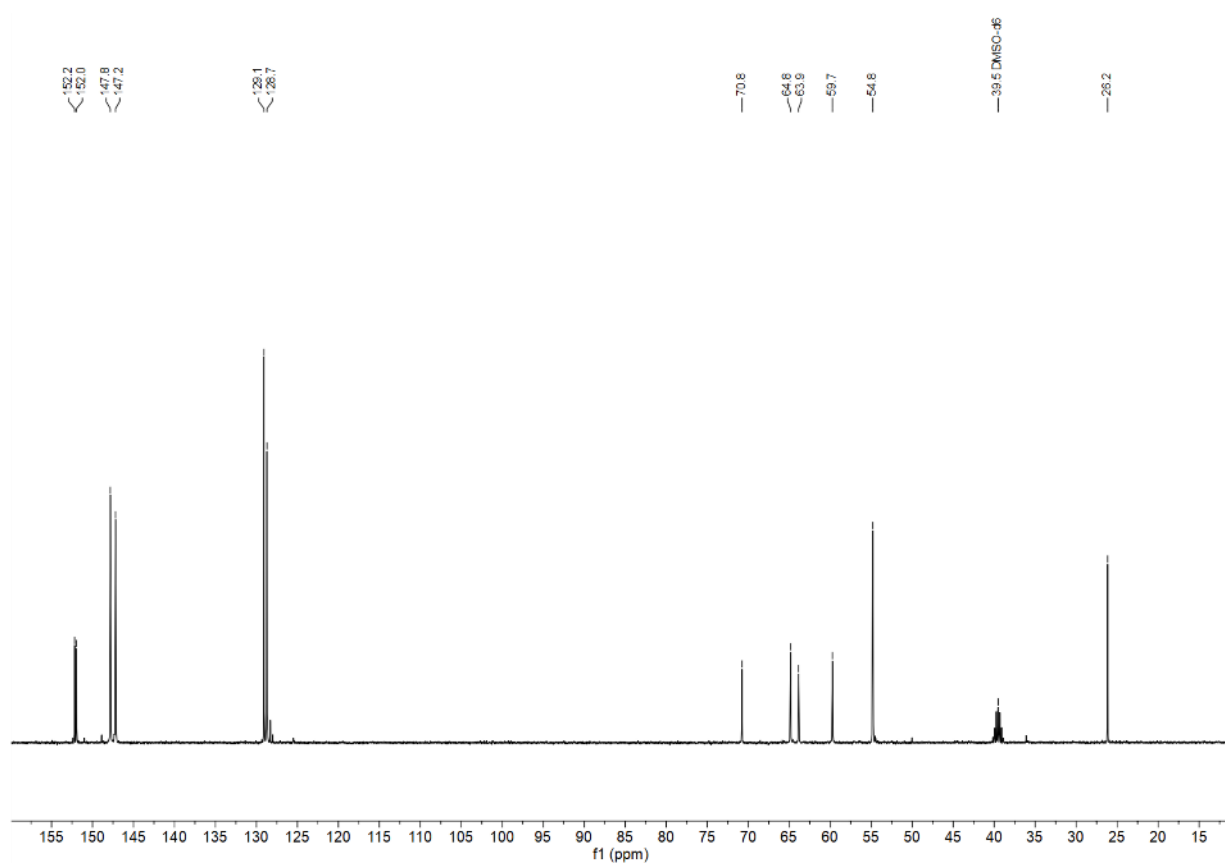
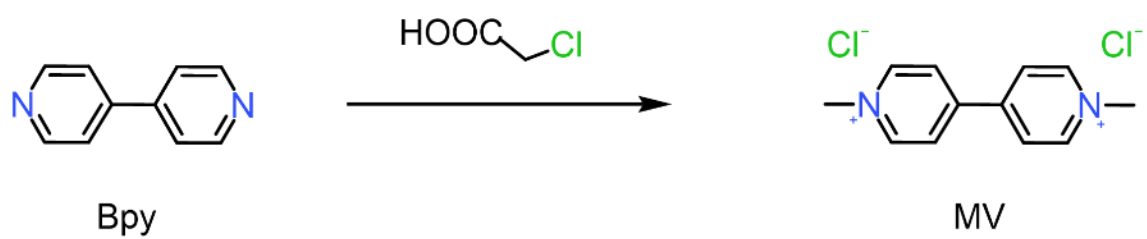
A**B**

Figure S4. NMR spectra of OH-bisNV. (A) ^1H NMR (D_2O); (B) ^{13}C NMR (D_2O with a drop of $\text{DMSO-}d_6$).



Scheme S2. Synthesis protocol of MV.

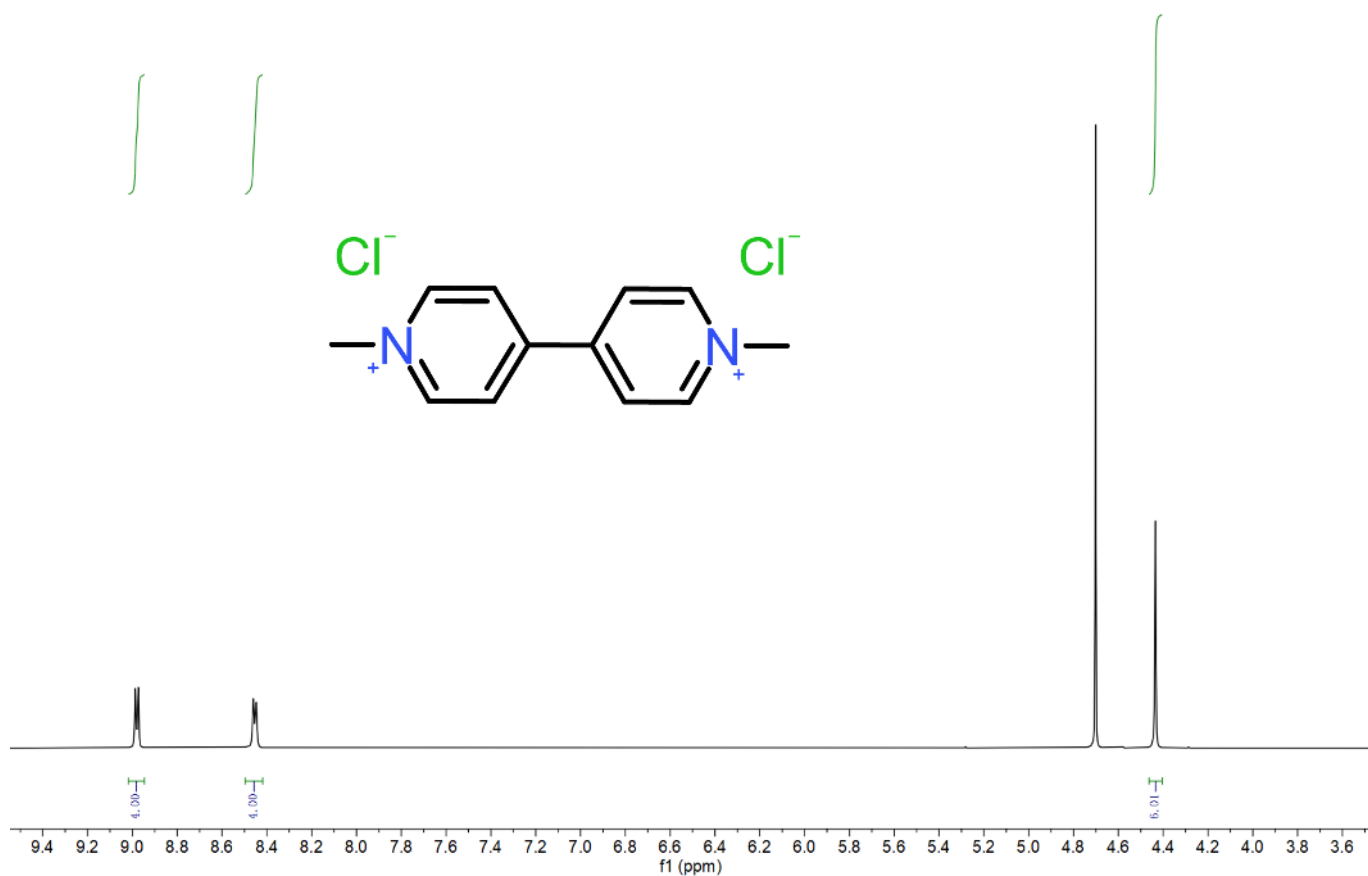
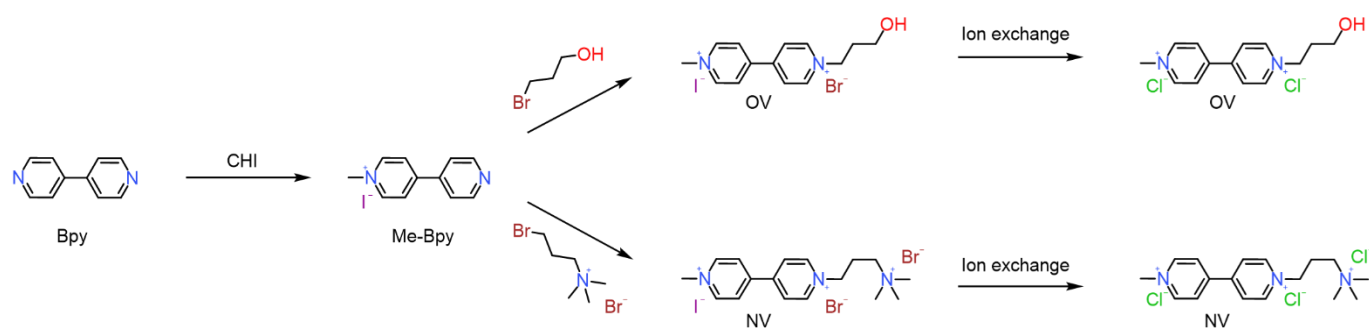


Figure S5. ^1H NMR spectrum of MV (D₂O).



Scheme S3. Synthesis protocol of OV and NV.

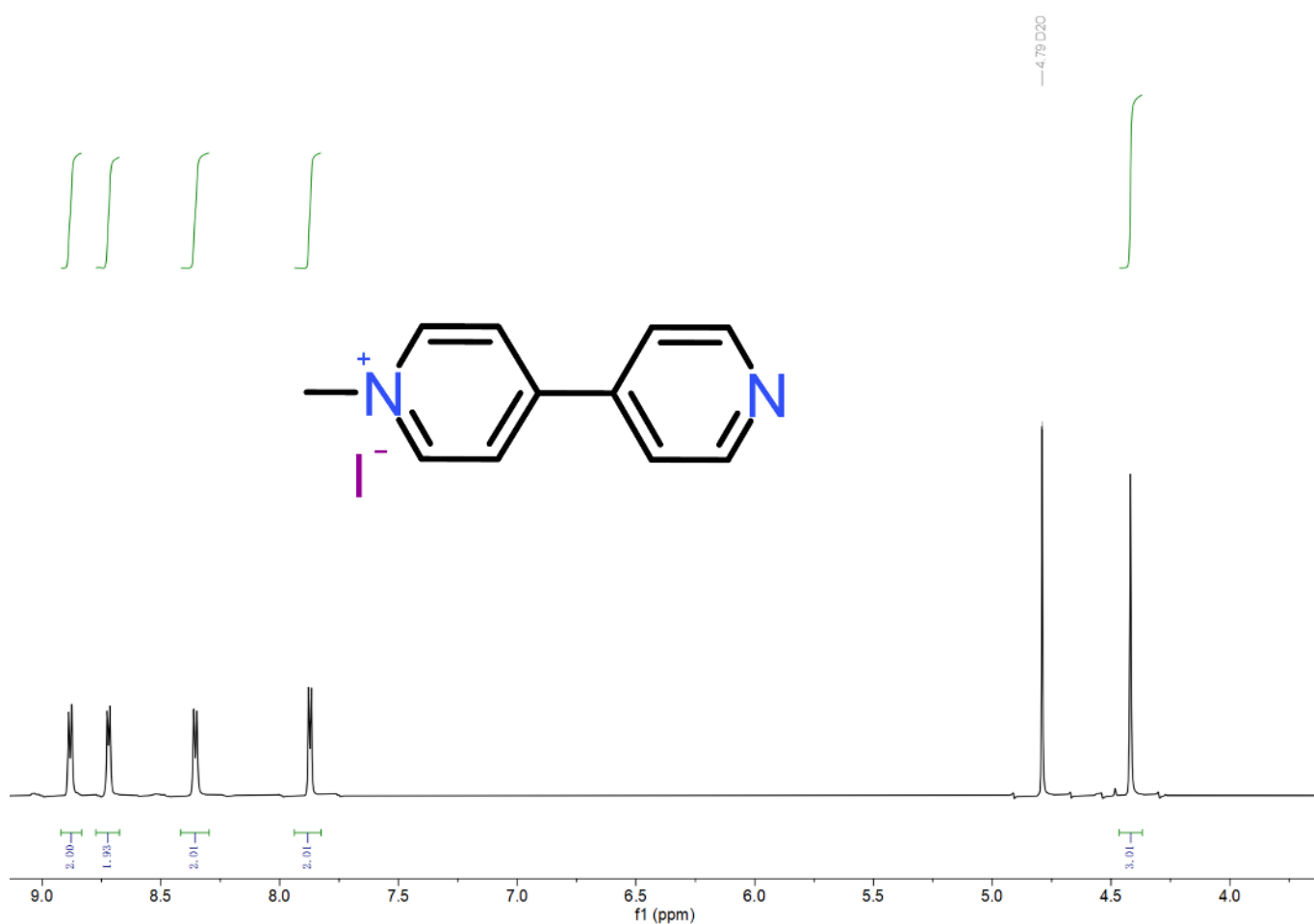


Figure S6. ^1H NMR spectrum of Me-Bpy (D_2O).

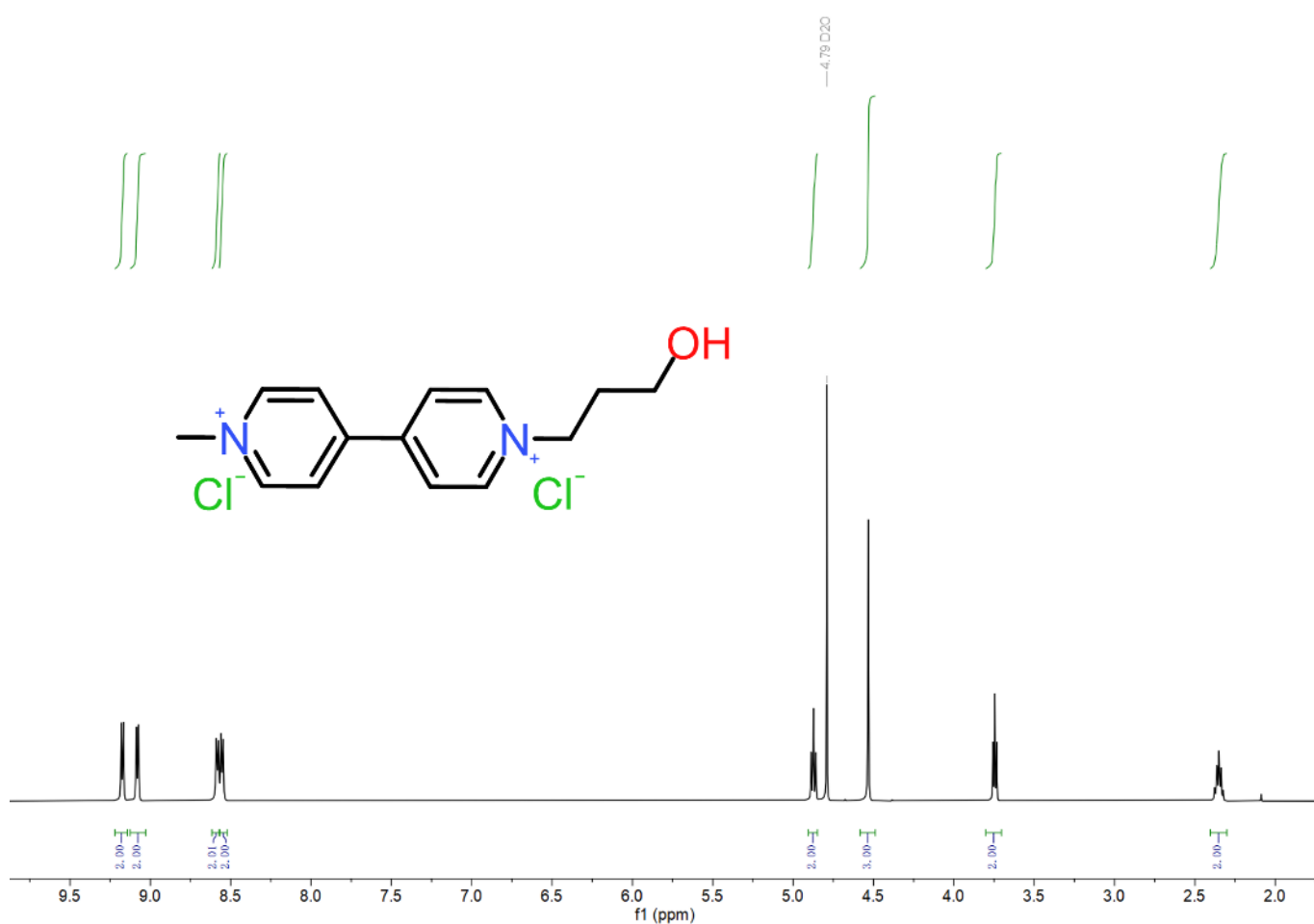


Figure S7. ^1H NMR spectrum of OV (D_2O).

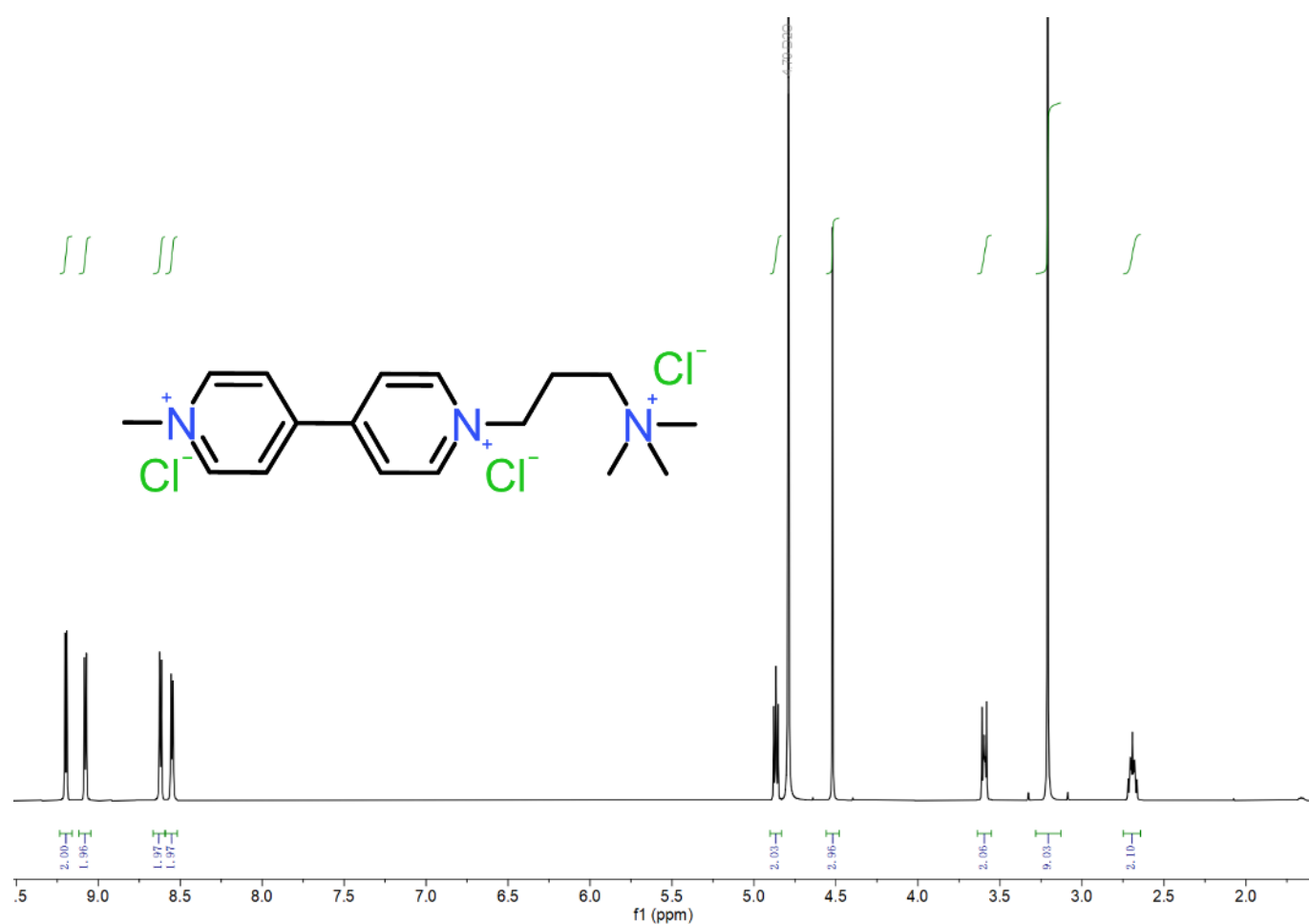


Figure S8. ^1H NMR spectrum of NV (D_2O).

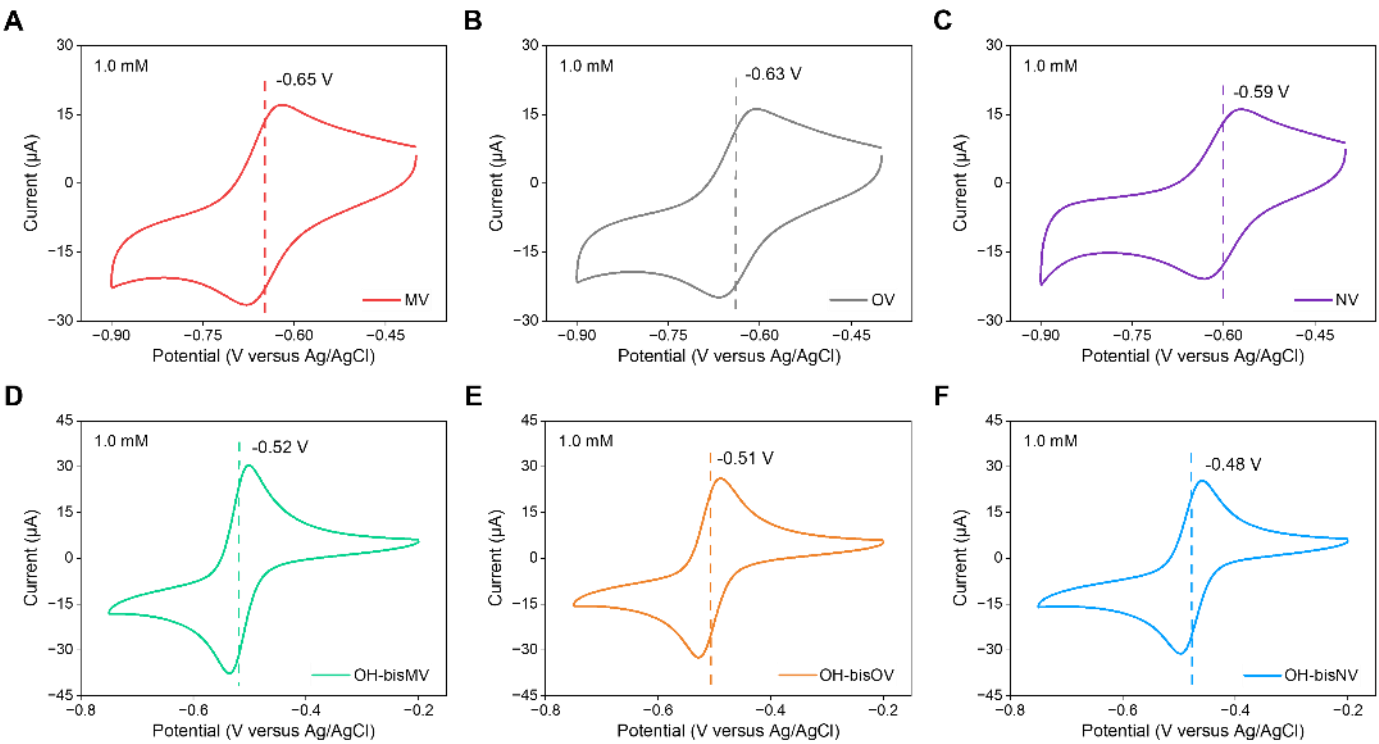
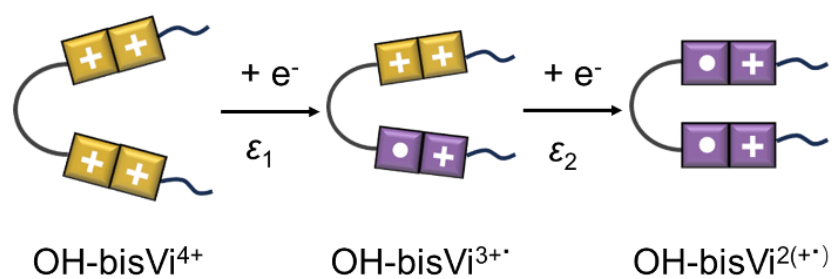


Figure S9. CVs of 1.0 mM negolyte at 100 mV s⁻¹ (supporting electrolyte: 0.50 M KCl). (A) MV; (B) OV; (C) NV; (D) OH-bisMV; (E) OH-bisOV; (F) OH-bisNV.



ε_1 : first-electron redox potential

ε_2 : second-electron redox potential

$(\varepsilon_1 < \varepsilon_2)$

Figure S10. Scheme of two-electron reduction of bis-viologen.

Table S1. Calculated electron energy (E_e) and free energy (E_{free}) of oxidized-state, one-electron reduced-state, and two-electron reduced-state bis-viologen at M06-2X/def2tzvp level.

Molecule	E_e / Hartree	E_{free} / Hartree
OH-bisMV ⁴⁺	-7332.593966	-7332.159684
OH-bisMV ³⁺	-6872.35444	-6871.921978
OH-bisMV ²⁽⁺⁾	-6412.118936	-6411.685751
OH-bisOV ⁴⁺	-11868.2892	-11867.74212
OH-bisOV ³⁺	-9294.050461	-9293.503842
OH-bisOV ²⁽⁺⁾	-6719.818669	-6719.27184
OH-bisNV ⁶⁺	-17213.99593	-17213.23636
OH-bisNV ⁵⁺	-14639.7625	-14639.00387
OH-bisNV ²⁽²⁺⁾	-12065.53164	-12064.77405

For reaction:

(1) $2 \text{ OH-bisMV}^{3+} \rightleftharpoons \text{OH-bisMV}^{4+} + \text{OH-bisMV}^{2(+)}$
 $\Delta G = [(-7332.159684) + (-6411.685751) - 2 \times (-6871.921978)] \text{ Hartree}$
 $= -0.001479 \text{ Hartree} \approx -0.93 \text{ kcal mol}^{-1}$

(2) $2 \text{ OH-bisOV}^{3+} \rightleftharpoons \text{OH-bisOV}^{4+} + \text{OH-bisOV}^{2(+)}$
 $\Delta G = [(-11867.74212) + (-6719.27184) - 2 \times (-9293.503842)] \text{ Hartree}$
 $= -0.006276 \text{ Hartree} \approx -3.94 \text{ kcal mol}^{-1}$

(3) $2 \text{ OH-bisNV}^{5+} \rightleftharpoons \text{OH-bisOV}^{6+} + \text{OH-bisOV}^{2(2+)}$
 $\Delta G = [(-17213.23636) + (-12064.77405) - 2 \times (-14639.00387)] \text{ Hartree}$
 $= -0.00267 \text{ Hartree} \approx -1.68 \text{ kcal mol}^{-1}$

According to above results, it is a thermodynamically spontaneous process that the one-electron reduced-state bis-viologen can disproportionate into the two-electron reduced-state bis-viologen and oxidized-state bis-viologen. It means that one bis-viologen can obtain two electrons simultaneously instead of one electron during reduction, and thus forms a pancake bond.

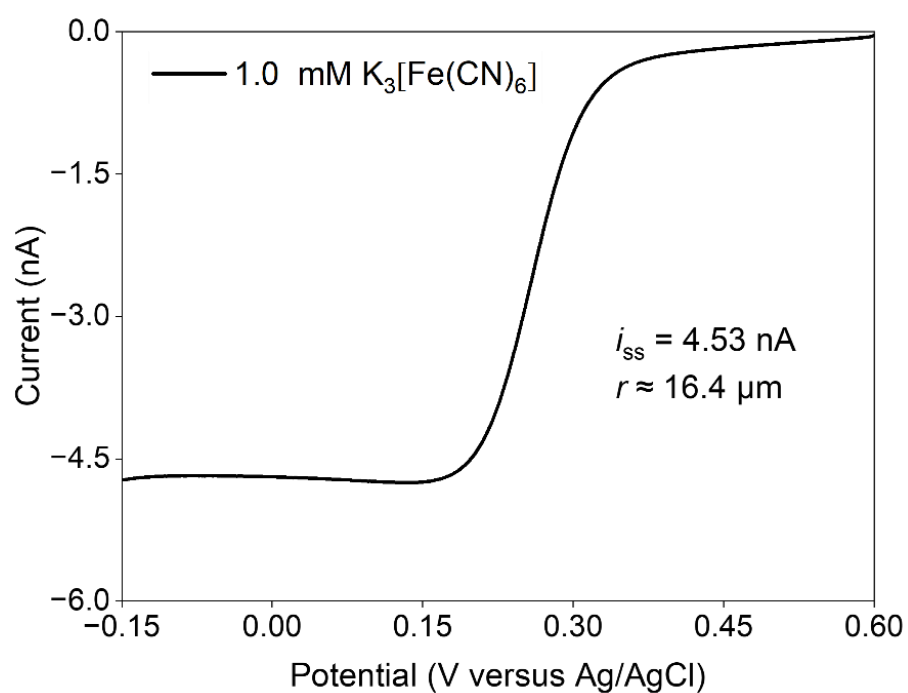


Figure S11. LSV of 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ (supporting electrolyte: 0.50 M KCl).

LSV test of 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution was performed on a microelectrode, as shown in Figure S11. The steady state current of 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ is 4.53 nA, and thus the radius of the microelectrode is calculated to be $\sim 16.4 \text{ }\mu\text{m}$.

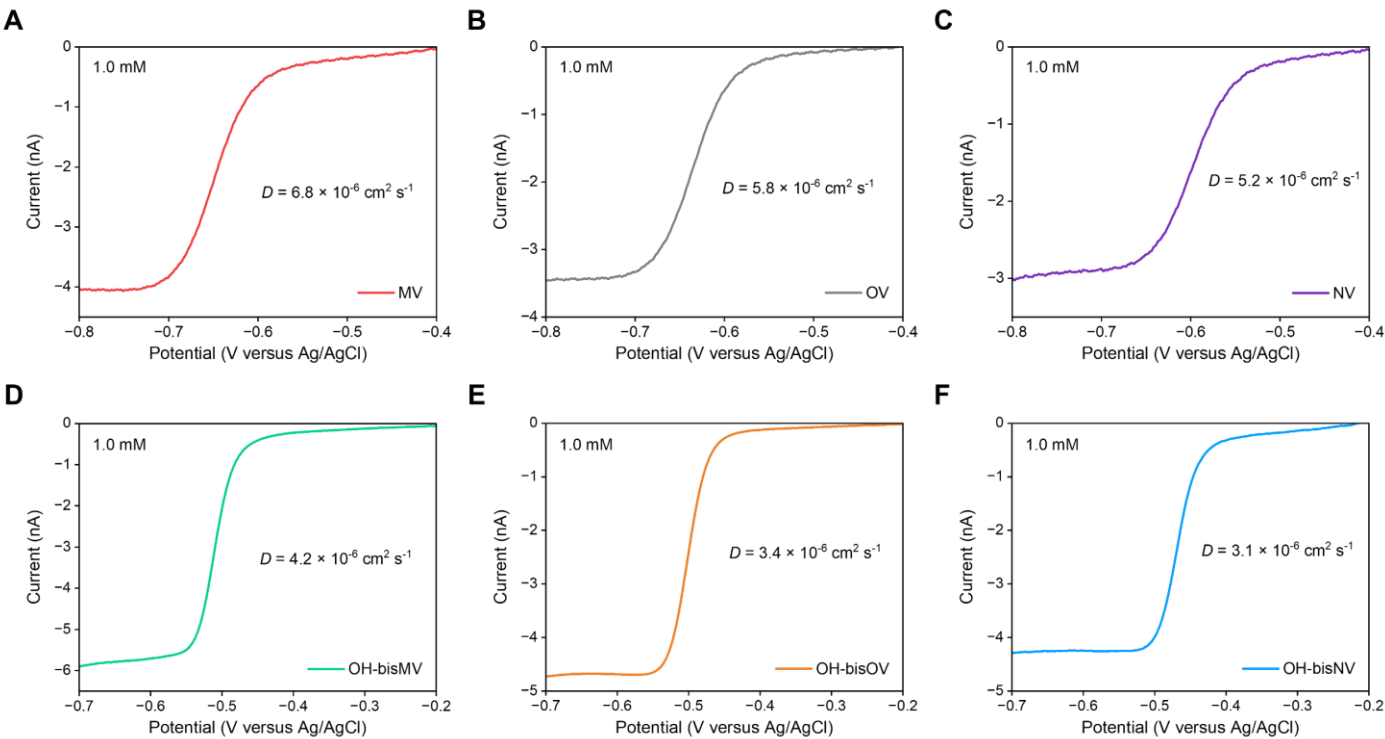


Figure S12. LSVs of 1.0 mM negolyt at 50 mV s⁻¹ (supporting electrolyte: 0.50 M KCl). (A) MV; (B) OV; (C) NV; (D) OH-bisMV; (E) OH-bisOV; (F) OH-bisNV.

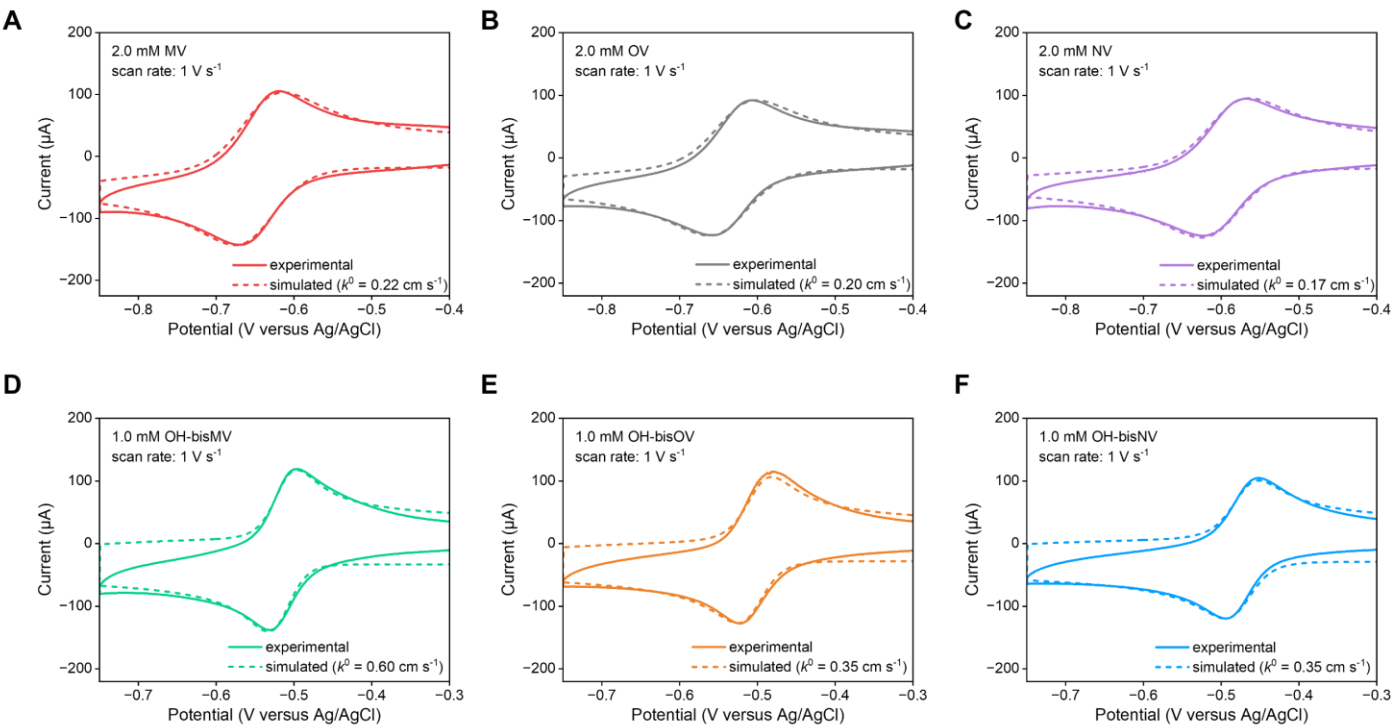


Figure S13. Electrochemical digital simulations of negolyte at 1 V s⁻¹ (supporting electrolyte: 0.50 M KCl). (A) 2.0 mM MV; (B) 2.0 mM OV; (C) 2.0 mM NV; (D) 1.0 mM OH-bisMV; (E) 1.0 mM OH-bisOV; (F) 1.0 mM OH-bisNV.

Table S2. Calculated Gibbs free energy (ΔG_e^0), inner reorganization energy (λ_{in}) and outer reorganization energy (λ_{out}) of half-reaction at M06-2X/def2tzvp level.

Half-reaction	ΔG_e^0 / eV	λ_{in} / eV	λ_{out} / eV
$MV^{+\cdot} \rightarrow MV^{2+}$	3.68	0.28	0.96
$OV^{+\cdot} \rightarrow OV^{2+}$	3.82	0.27	0.94
$NV^{2+\cdot} \rightarrow NV^{3+}$	3.84	0.34	0.93
$OH\text{-bis}MV^{2(+\cdot)} \rightarrow OH\text{-bis}MV^{3+\cdot}$	3.87	0.18	0.78
$OH\text{-bis}OV^{2(+\cdot)} \rightarrow OH\text{-bis}OV^{3+\cdot}$	3.91	0.15	0.76
$OH\text{-bis}NV^{2(2+\cdot)} \rightarrow OH\text{-bis}NV^{5+\cdot}$	3.89	0.24	0.75
$O_2 \rightarrow O_2^{\cdot-}$	-4.03	0.54	1.75

The bis-viologens have lower λ_{in} and λ_{out} than those of mono-viologens. As the viologen systems obey an adiabatic electron transfer process on the surface of glassy carbon electrode,^{S1} the smaller recombination energy results in a larger k^0 .

Table S3. Summary of the physiochemical properties of bis-viologens and mono-viologens.					
Molecule	Solubility (M)	Electron number	$E_{1/2}$ (V versus Ag/AgCl)	D (cm ² s ⁻¹)	k^0 (cm s ⁻¹)
MV	2.5	1	-0.65	6.8×10 ⁻⁶	0.22
OV	2.6	1	-0.63	5.8×10 ⁻⁶	0.20
NV	1.8	1	-0.59	5.2×10 ⁻⁶	0.17
OH-bisMV	1.9	2	-0.52	4.2×10 ⁻⁶	0.60
OH-bisOV	2.0	2	-0.51	3.4×10 ⁻⁶	0.35
OH-bisNV	1.3	2	-0.48	3.1×10 ⁻⁶	0.35

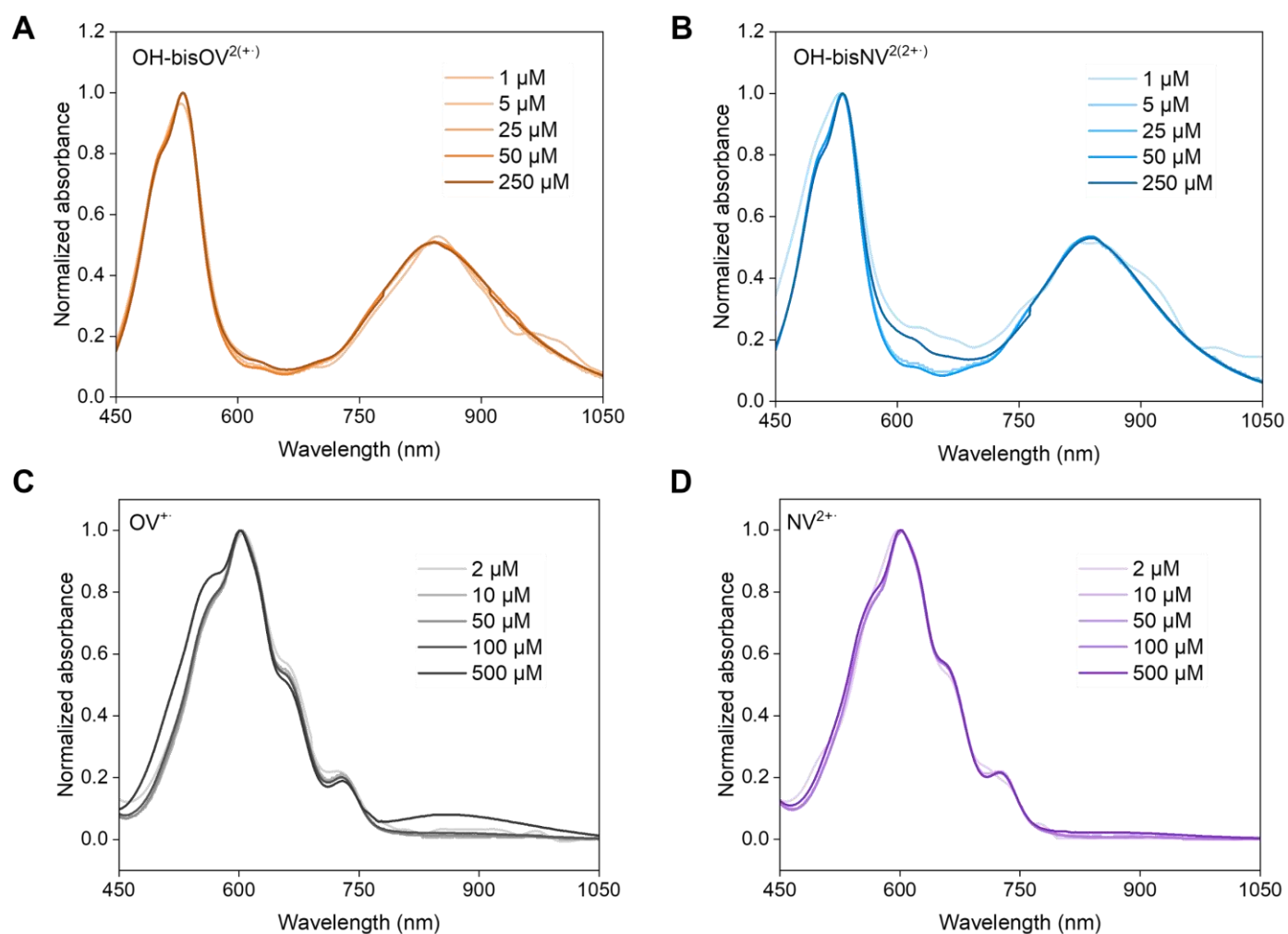


Figure S14. UV-vis-NIR spectra of negolyte at different concentrations. (A) OH-bisOV²⁽⁺⁾; (B) OH-bisNV²⁽²⁺⁾; (C) OV⁺ and (D) NV²⁺.

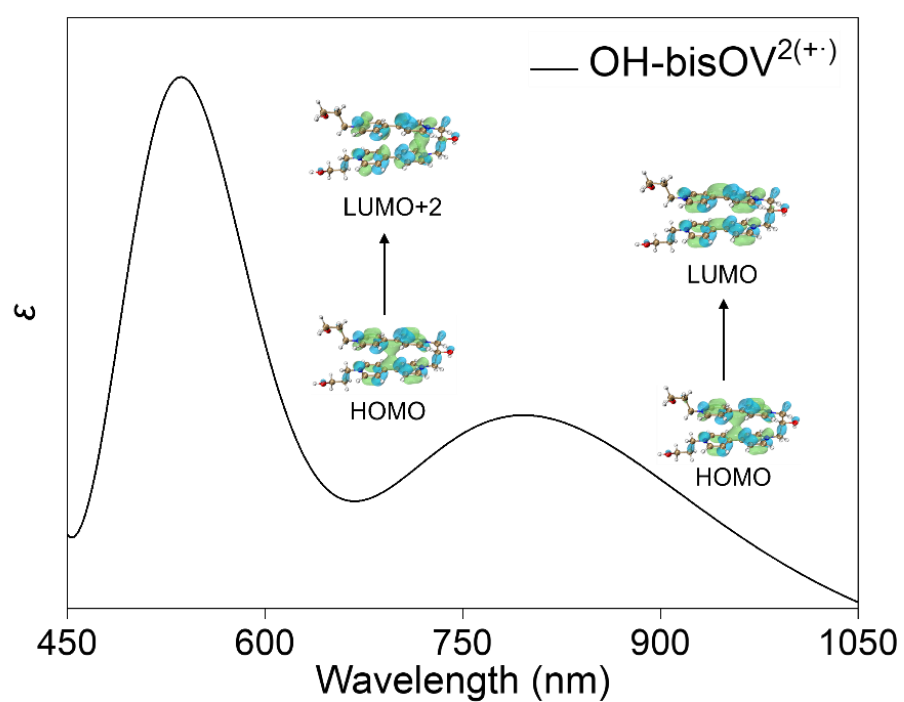
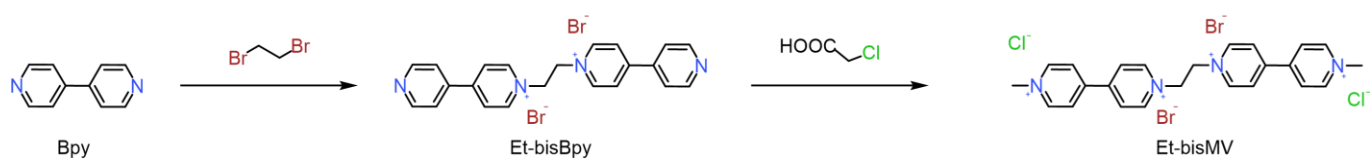


Figure S15. Calculated electronic spectrum and corresponding transition.

The electronic spectrum of OH-bisOV^{2(+·)} is calculated as an example. It is seen that the simulated electronic spectrum of singlet folda-structure has two absorption peaks within the range of 450 to 1050 nm, which are similar to the experimental result. The two absorption peaks correspond to the S0-S1 (mainly contributed by HOMO-LUMO) and S0-S4 (mainly contributed by HOMO-LUMO+2) leaps, respectively.



Scheme S4. Synthesis protocol of Et-bisMV.

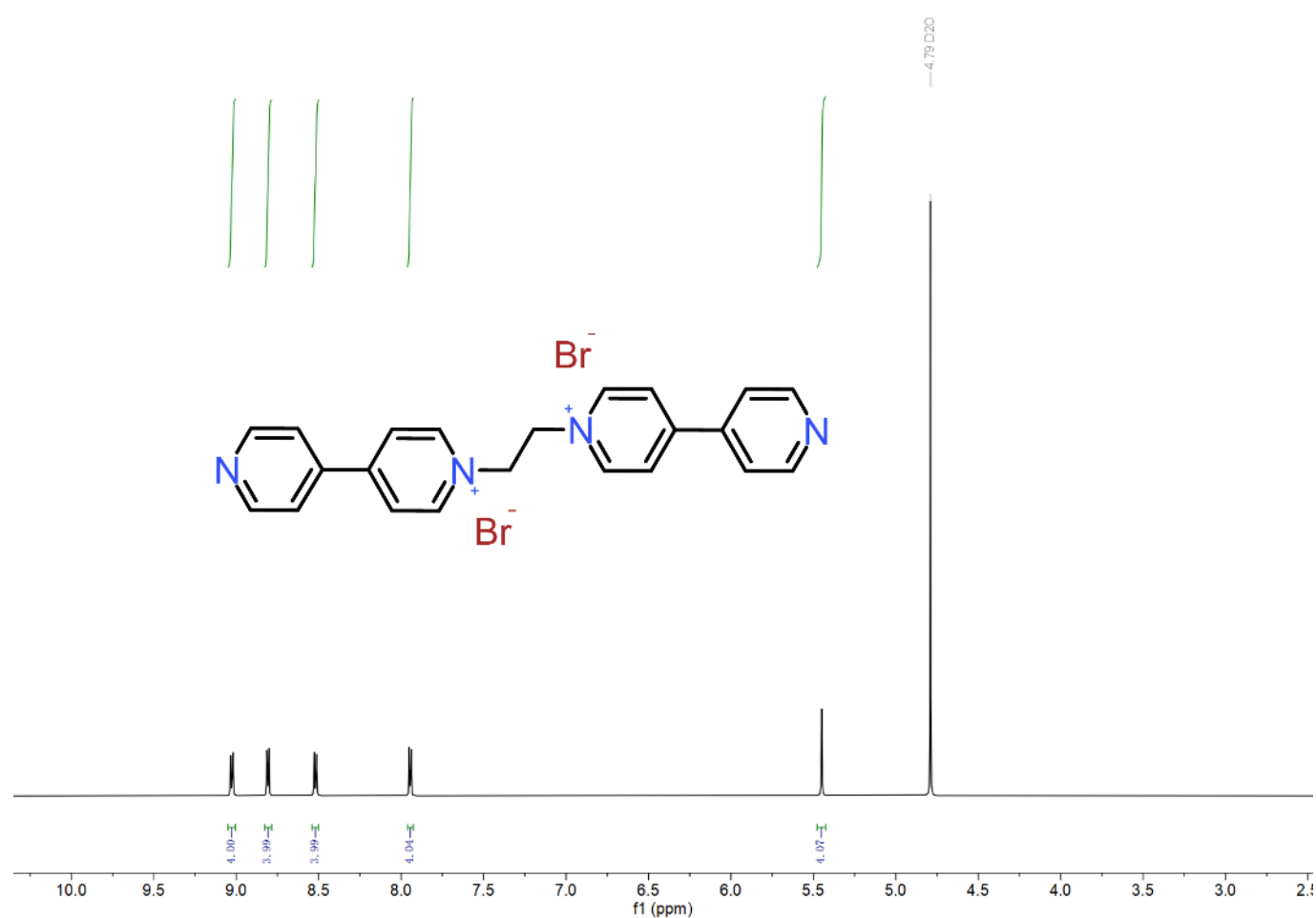


Figure S16. ^1H NMR spectrum of Et-bisBpy (D_2O).

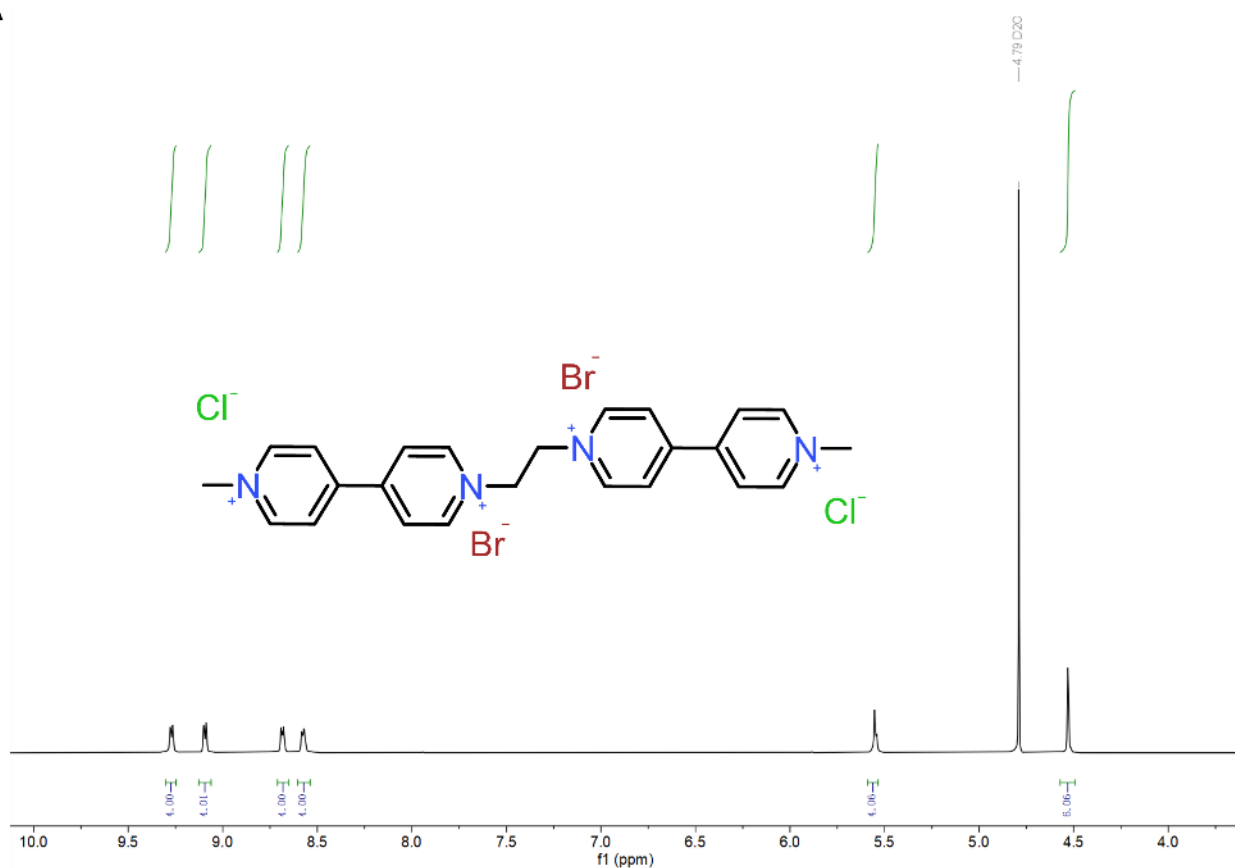
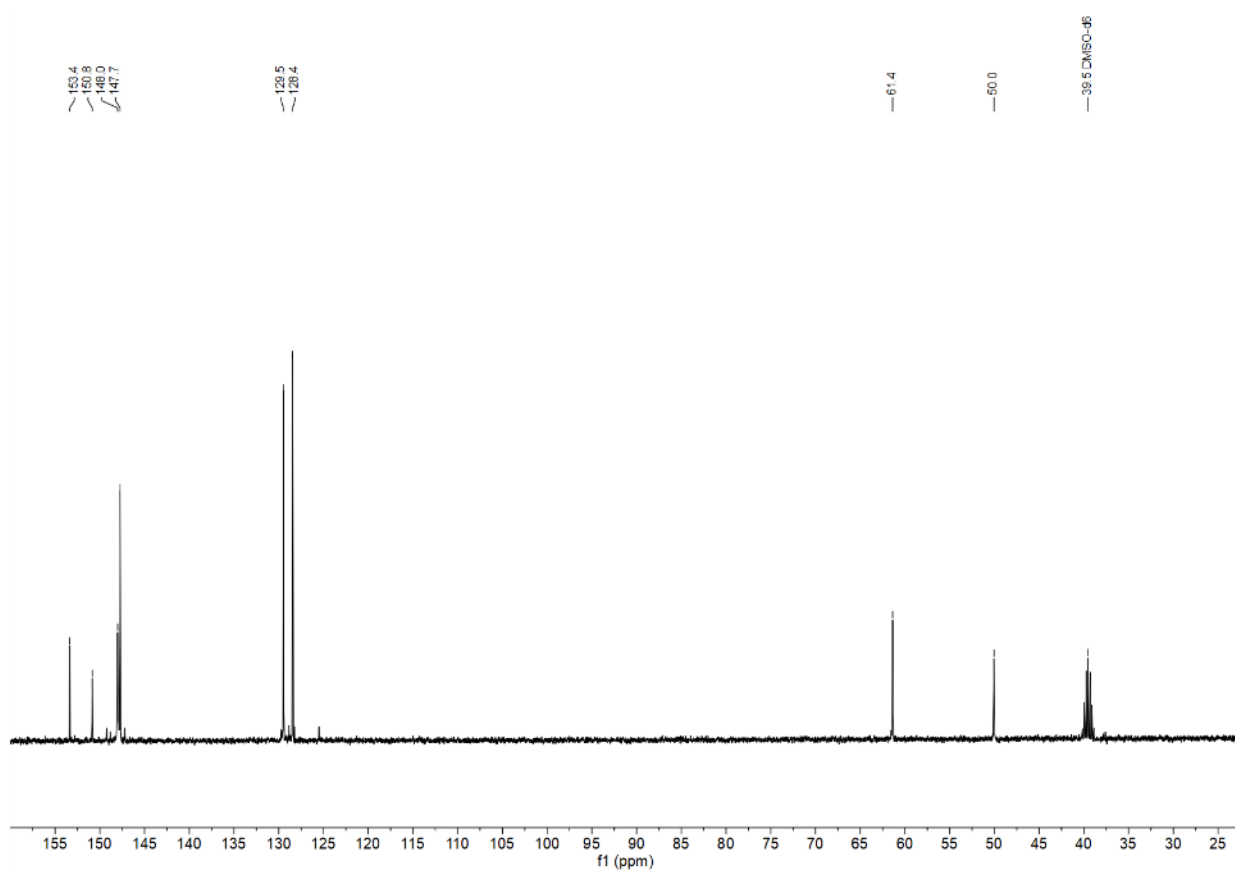
A**B**

Figure S17. NMR spectra of Et-bisMV. (A) ^1H NMR (D₂O); (B) ^{13}C NMR (D₂O with a drop of DMSO-*d*₆).

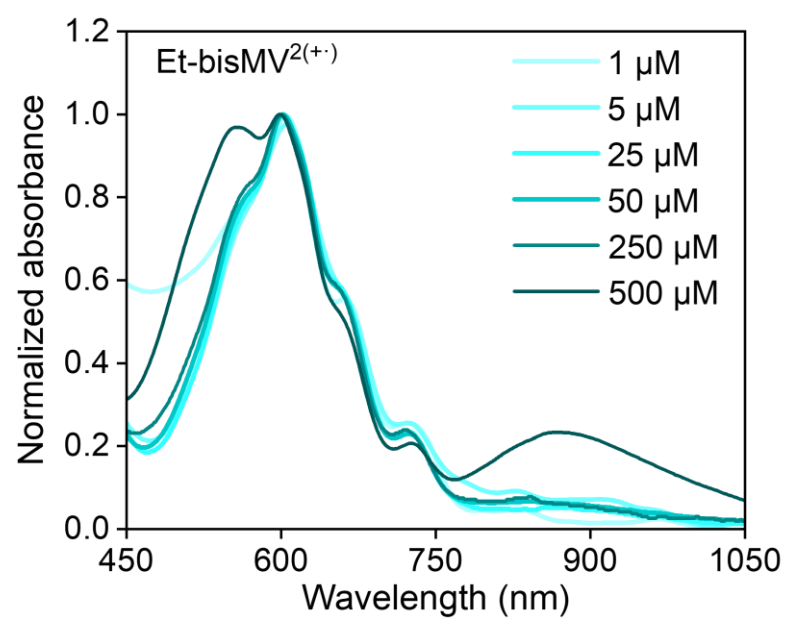


Figure S18. UV-vis-NIR spectra of Et-bisMV²⁽⁺⁾ at different concentrations.

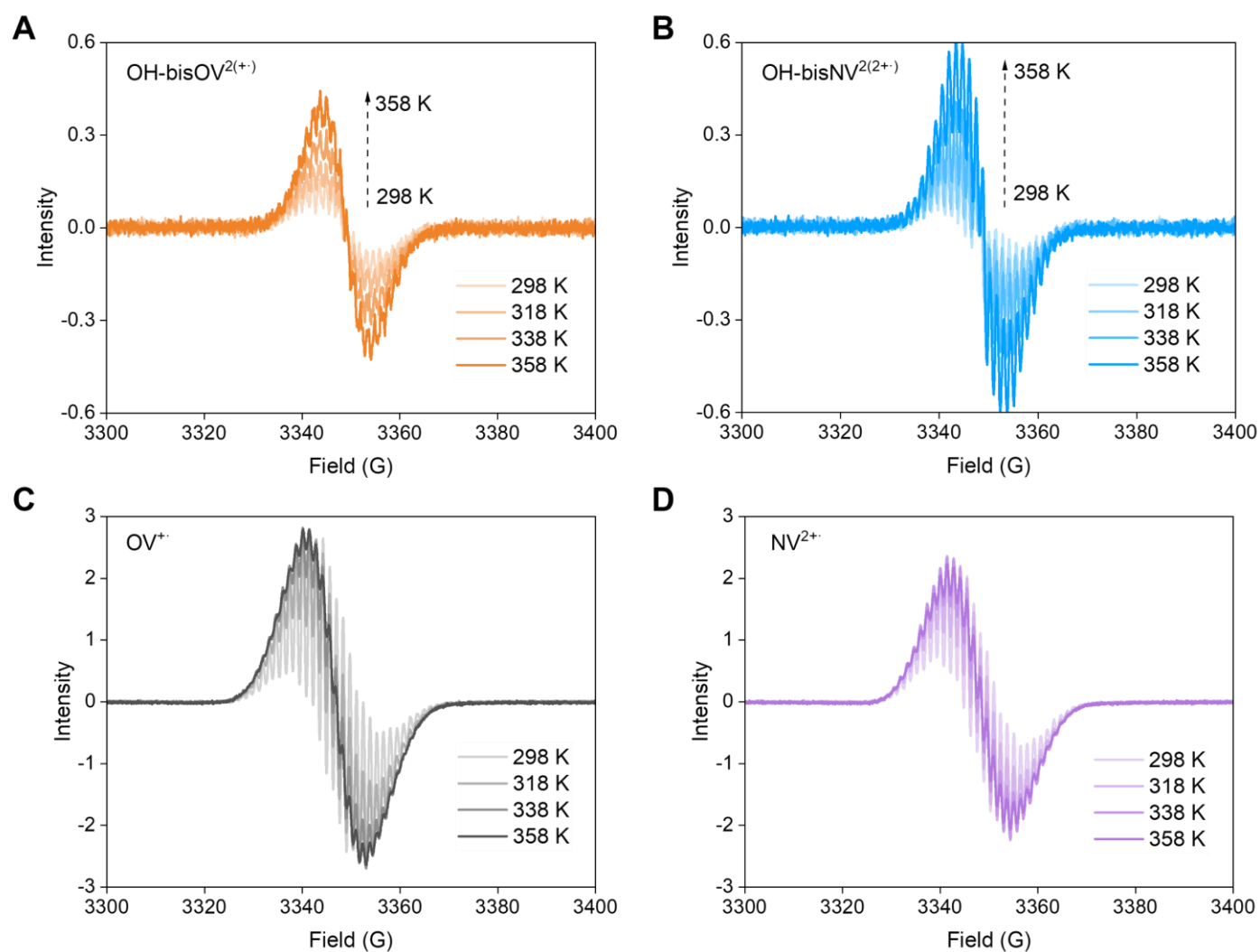


Figure S19. Variable-temperature EPR spectra of 2.0 mM negolyte. (A) OH-bisOV²⁽⁺⁾; (B) OH-bisNV²⁽²⁺⁾; (C) OV⁺ and (D) NV²⁺.

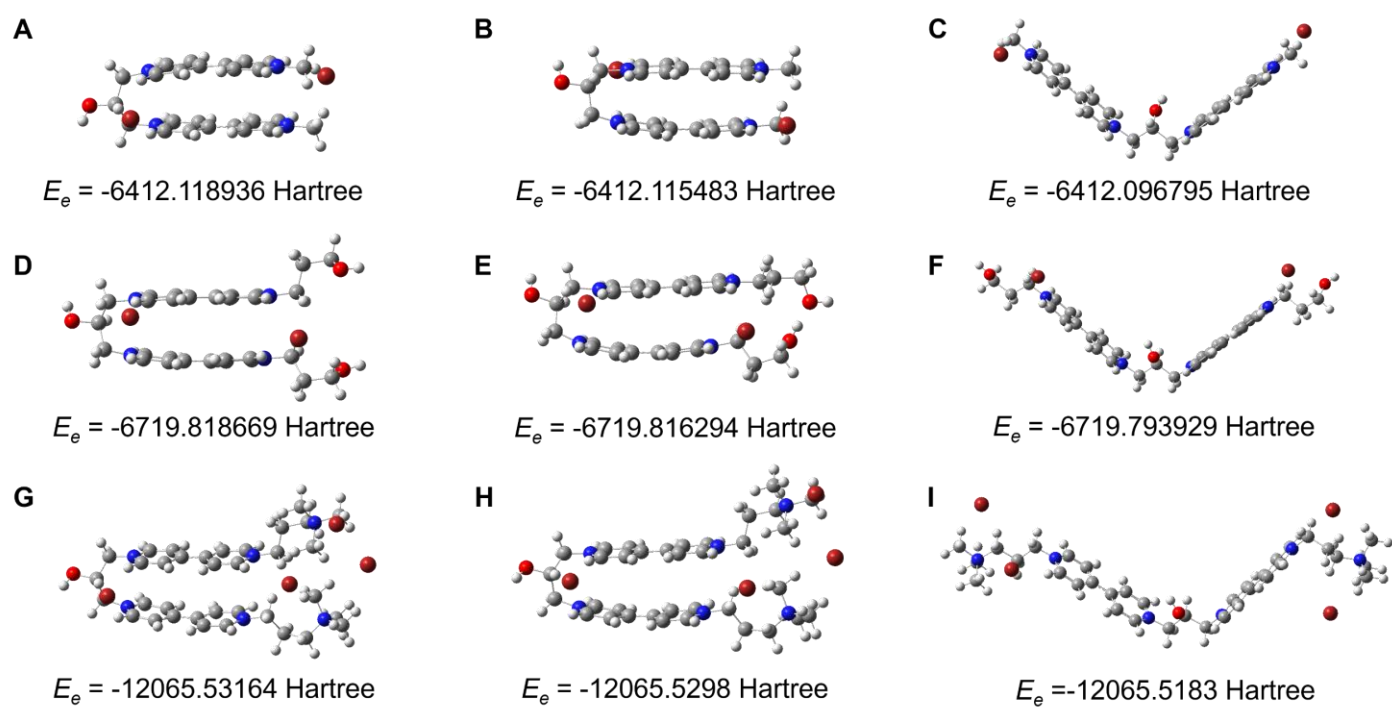


Figure S20. Calculated E_e of different conformations of reduced-state bis-viologens. The calculated E_e of (A) singlet folded, (B) triplet folded and (C) unfolded OH-bisMV²⁽⁺⁾; the calculated energy of (D) singlet folded, (E) triplet folded and (F) unfolded OH-bisOV²⁽⁺⁾; the calculated energy of (G) singlet folded, (H) triplet folded and (I) unfolded OH-bisNV²⁽²⁺⁾.

Table S4. Calculated E_e and E_{free} of three possible conformations of bis-viologen at M06-2X/def2tzvp level, and their conformation Boltzmann distribution at 298 K.

Conformation	E_e / Hartree	E_{free} / Hartree	Boltzmann distribution
singlet folded OH-bisMV ^{2(+·)}	-6412.118936	-6411.685751	98.17%
triplet folded OH-bisMV ^{2(+·)}	-6412.115483	-6411.681993	1.83%
unfolded OH-bisMV ^{2(+·)}	-6412.096795	-6411.67391	0.00%
singlet folded OH-bisOV ^{2(+·)}	-6719.818669	-6719.27184	99.88%
triplet folded OH-bisOV ^{2(+·)}	-6719.816294	-6719.265514	0.12%
unfolded OH-bisOV ^{2(+·)}	-6719.793929	-6719.253917	0.00%
singlet folded OH-bisNV ^{2(2+·)}	-12065.53164	-12064.77405	88.97%
triplet folded OH-bisNV ^{2(2+·)}	-12065.5298	-12064.77208	11.00%
unfolded OH-bisNV ^{2(2+·)}	-12065.5183	-12064.76654	0.03%

It is seen from Figure S20 and Table S4, the singlet folded conformation of OH-bisMV^{2(+·)}, OH-bisOV^{2(+·)} and OH-bisNV^{2(2+·)} has lower free energy compared with other two conformations, indicating that the singlet folded conformation is more favored.

Table S5. Calculated Gibbs free energy (ΔG^0), reorganization energy (λ), activation barrier free energy ($\Delta G_{RC}^\ddagger$) of the electron transfer reaction between reduced-state viologen molecules with O₂.

Reaction	ΔG^0 / eV	λ / eV	$\Delta G_{RC}^\ddagger$ / eV
$MV^{+\cdot} + O_2 \rightarrow MV^{2+} + O_2^{\cdot-}$	-0.35	3.53	0.72
$OV^{+\cdot} + O_2 \rightarrow OV^{2+} + O_2^{\cdot-}$	-0.21	3.51	0.77
$NV^{2+\cdot} + O_2 \rightarrow NV^{3+} + O_2^{\cdot-}$	-0.20	3.57	0.79
$OH\text{-bis}MV^{2(+\cdot)} + O_2 \rightarrow OH\text{-bis}MV^{3+\cdot} + O_2^{\cdot-}$	-0.16	3.25	0.73
$OH\text{-bis}OV^{2(+\cdot)} + O_2 \rightarrow OH\text{-bis}OV^{3+\cdot} + O_2^{\cdot-}$	-0.12	3.20	0.74
$OH\text{-bis}NV^{2(2+\cdot)} + O_2 \rightarrow OH\text{-bis}NV^{5+\cdot} + O_2^{\cdot-}$	-0.14	3.28	0.75

Table S6. Boltzmann distribution of the clustered O₂+MV⁺ configurations at 298 K and corresponding |H_{DA}|.

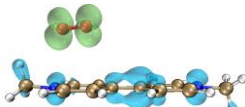
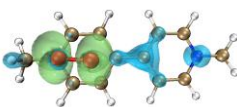
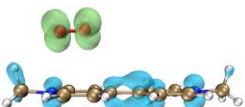
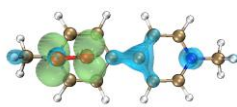
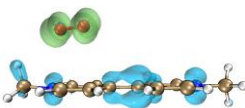
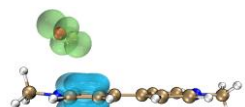
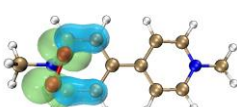
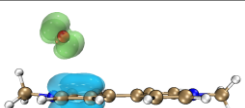
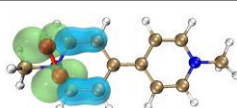
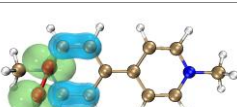
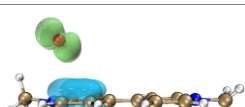
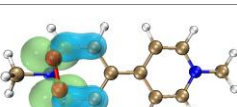
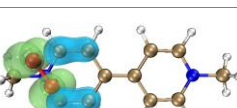
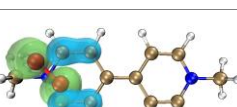
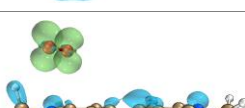
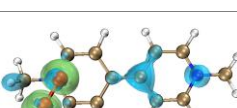
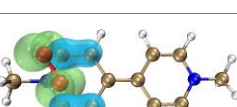
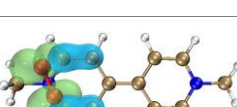
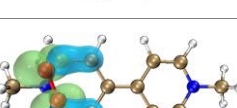
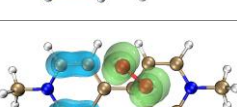
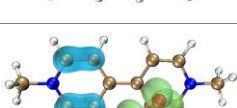
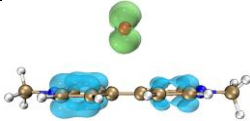
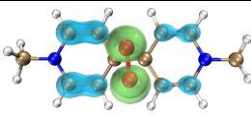
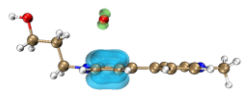
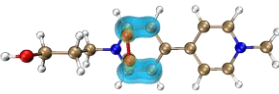
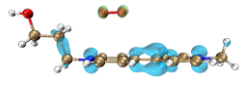
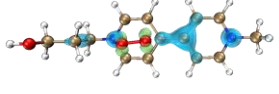
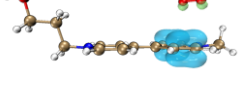
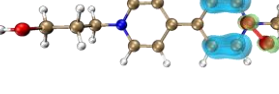
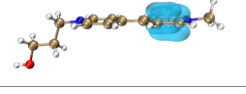
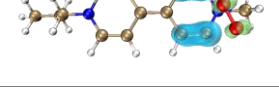
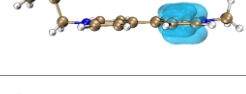
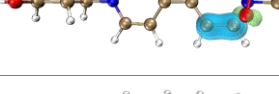
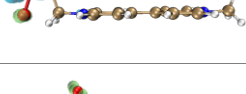
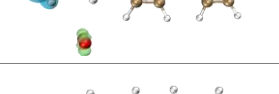
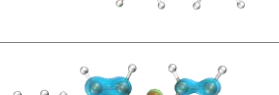
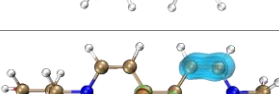
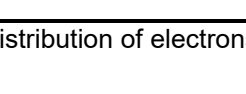
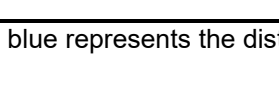
Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
1			10.56%	0.664
2			8.68%	0.355
3			8.48%	0.301
4			7.54%	0.310
5			7.50%	0.311
6			6.49%	0.312
7			6.37%	0.323
8			6.33%	0.301
9			5.82%	0.288
10			5.81%	0.288
11			5.79%	0.295
12			5.59%	0.308
13			5.20%	0.312
14			3.52%	0.187
15			3.48%	0.190

Table S6 (continued). Boltzmann distribution of the clustered O₂+MV⁺ configurations at 298 K and corresponding |H_{DA}|.

Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
16			2.84%	0.360

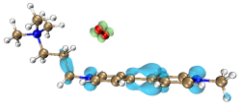
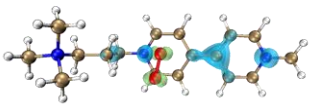
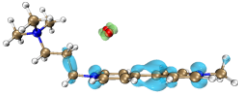
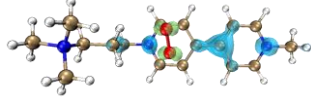
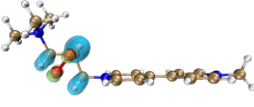
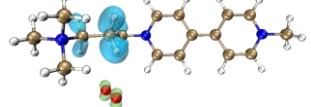
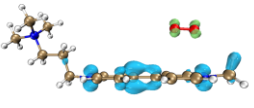
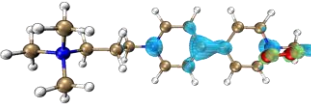
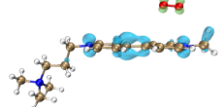
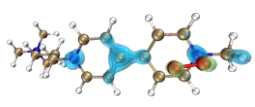
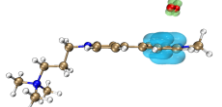
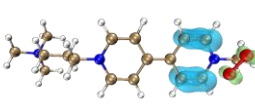
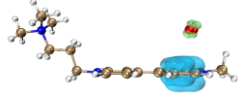
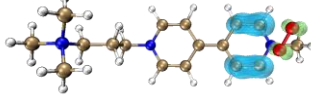
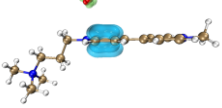
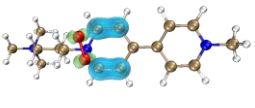
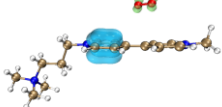
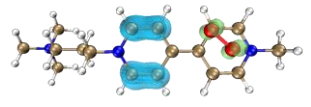
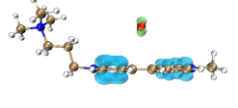
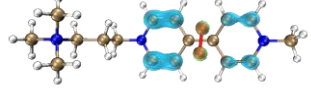
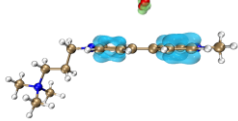
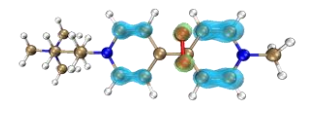
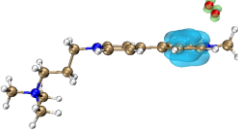
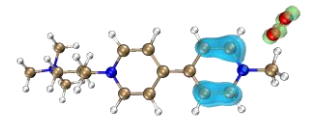
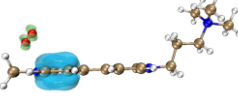
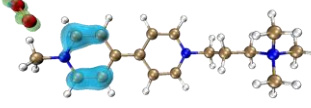
^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

Table S7. Boltzmann distribution of the clustered O₂+OV⁺ configurations at 298 K and corresponding |H_{DA}|.

Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
1			31.49%	0.36
2			23.14%	0.32
3			11.03%	0.33
4			8.03%	0.44
5			7.81%	0.34
6			4.43%	1.63
7			4.42%	0.43
8			3.64%	0.42
9			3.27%	0.65
10			2.74%	0.2

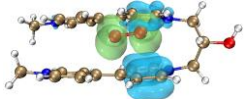
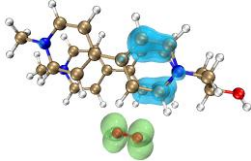
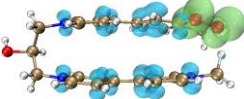
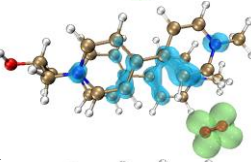
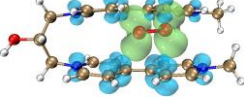
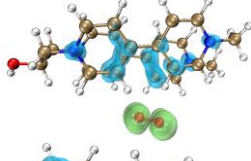
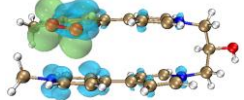
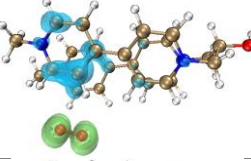
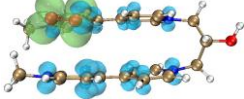
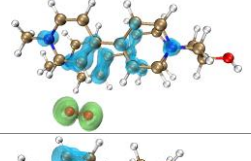
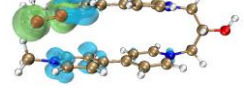
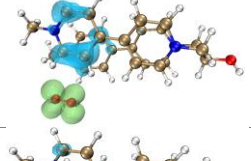
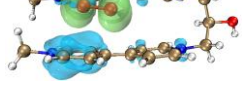
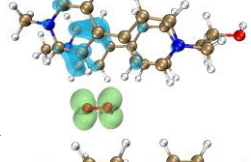
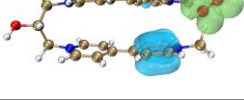
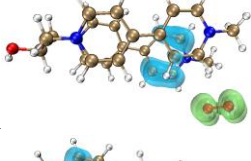
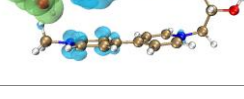
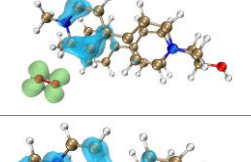
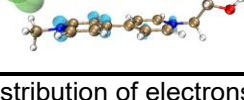
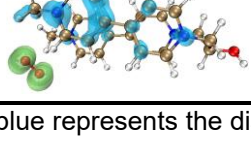
^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

Table S8. Boltzmann distribution of the clustered O₂+NV²⁺ configurations at 298 K and corresponding $|H_{DA}|$.

Configuration	Front view ^a	Top view	Boltzmann distribution	$ H_{DA} $ / eV
1			31.92%	1.25
2			27.03%	1.15
3			13.35%	0.33
4			4.88%	1.02
5			4.66%	0.71
6			4.64%	0.36
7			4.26%	0.76
8			2.09%	0.57
9			1.87%	0.21
10			1.84%	1.02
11			1.76%	0.60
12			0.86%	0.19
13			0.84%	0.25

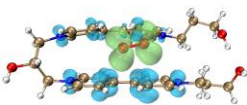
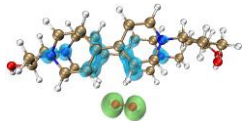
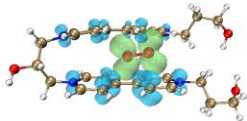
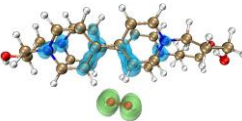
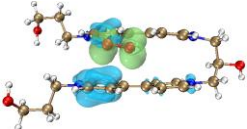
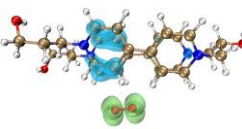
^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

Table S9. Boltzmann distribution of the clustered O₂+OH-bisMV²⁽⁺⁾ configurations at 298 K and corresponding |H_{DA}|.

Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
1			24.36%	0.055
2			16.00%	0.054
3			10.51%	0.218
4			10.44%	0.207
5			10.22%	0.078
6			10.13%	0.088
7			9.14%	0.035
8			4.71%	0.076
9			3.55%	0.116
10			0.94%	0.032

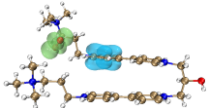
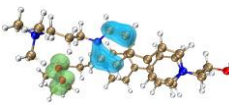
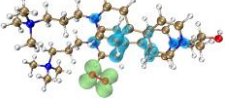
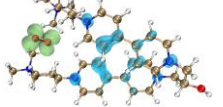
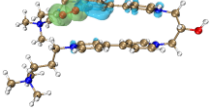
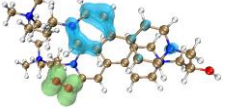
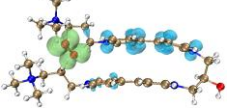
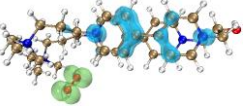
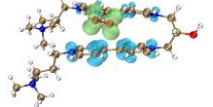
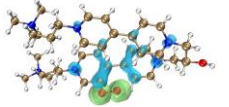
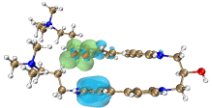
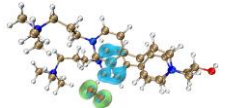
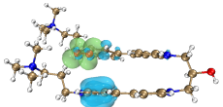
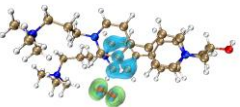
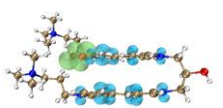
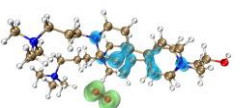
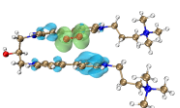
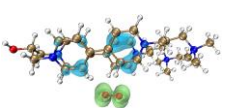
^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

Table S10. Boltzmann distribution of the clustered O₂+OH-bisOV²⁽⁺⁾ configurations at 298 K and corresponding |H_{DA}|.

Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
1			99.45%	0.097
2			0.48%	0.092
3			0.07%	0.101

^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

Table S11. Boltzmann distribution of the clustered O₂+OH-bisNV^{2(2+·)} configurations at 298 K and corresponding |H_{DA}|.

Configuration	Front view ^a	Top view	Boltzmann distribution	H _{DA} / eV
1			45.8%	0.063
2			12.86%	0.34
3			17.3%	0.058
4			7.74%	1.215
5			4.55%	0.181
6			3.18%	0.966
7			3.49%	0.332
8			2.39%	0.357
9			2.04%	0.152
10			0.65%	0.181

^aNote: Green represents the distribution of electrons and blue represents the distribution of holes on the isosurface.

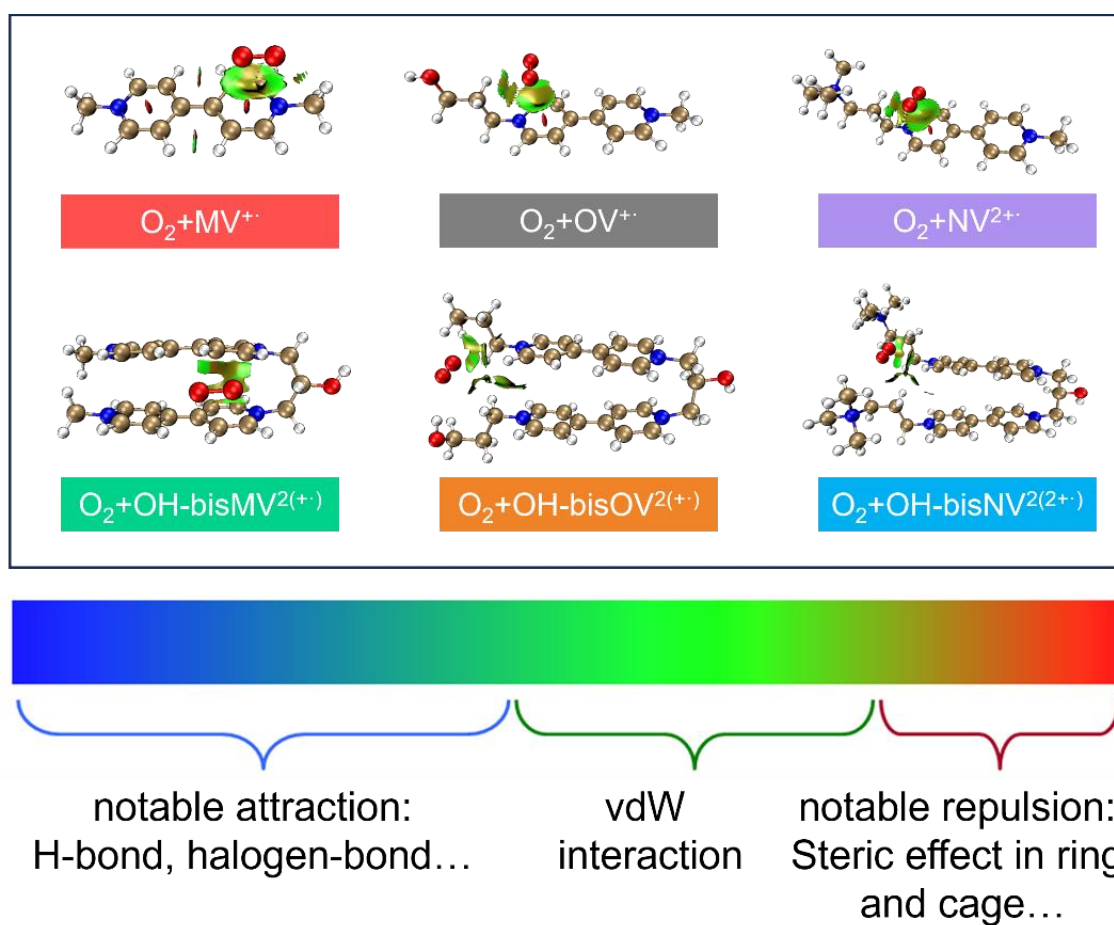


Figure S21. Noncovalent interaction (NCI) analysis. NCI of $O_2+MV^{+\bullet}$, $O_2+OV^{+\bullet}$, $O_2+NV^{2+\bullet}$, $O_2+OH\text{-bis}MV^{2(+\bullet)}$, $O_2+OH\text{-bis}OV^{2(+\bullet)}$ and $O_2+OH\text{-bis}NV^{2(2+\bullet)}$; where the red, blue and green areas respectively represent the notable repulsion, notable attraction and *van der Waals* (*vdW*) interaction.^{S2, S3}

As demonstrated in Figure S21, the NCI between the reduced-state viologens and O_2 is predominantly green, indicating that the *vdW* interaction between the reduced-state viologens and O_2 is the primary interaction.

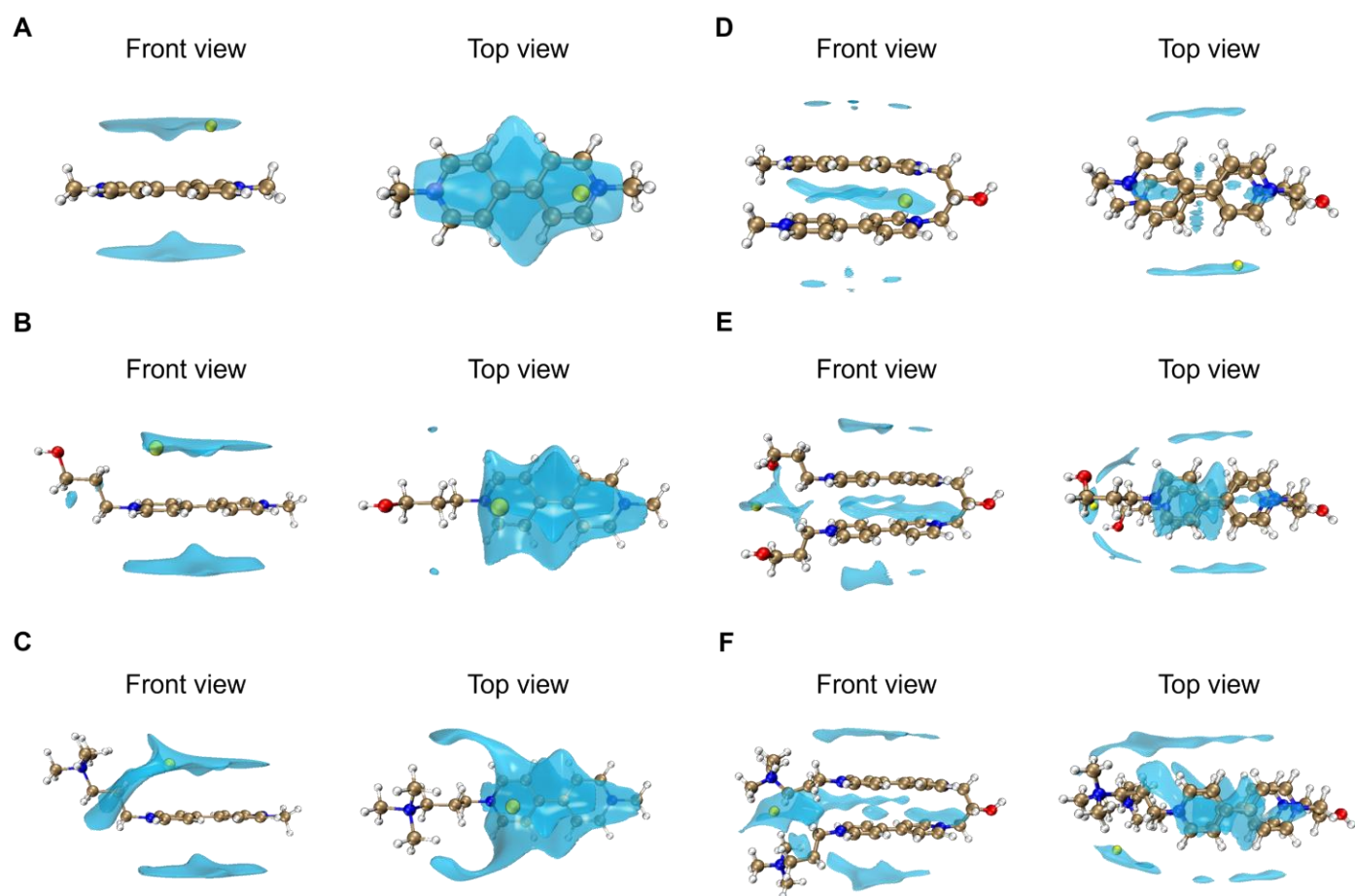


Figure 22. Calculated *vdW* potential energy surface. (A) MV^{+} ; (B) OV^{+} ; (C) NV^{2+} ; (D) $OH\text{-bis}MV^{2(+)}$; (E) $OH\text{-bis}OV^{2(+)}$ and (F) $OH\text{-bis}NV^{2(2+)}$. The yellow sphere represents minima.

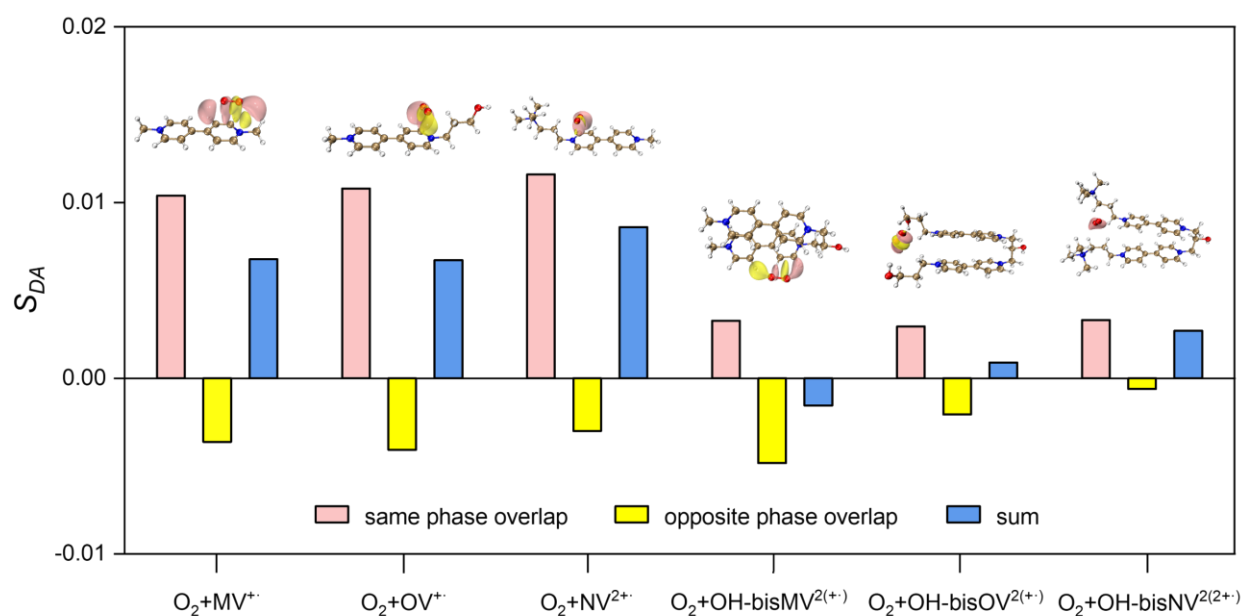


Figure S23. Calculated orbit overlap integral and corresponding cluster (note: here the absolute value of the sum value represents the whole overlap integral).

Table S12. Calculated singlet-triplet energy gap (ΔE_{S-T}) at the M06-2X/def2tzvp level.

Molecule	E_S / Hartree	E_T / Hartree	$\langle S^2 \rangle_S$	$\langle S^2 \rangle_T$	ΔE_{S-T} / eV
OH-bisMV ^{2(+·)}	-6412.118936	-6412.110442	0.7307	2.0291	-0.36
OH-bisOV ^{2(+·)}	-6719.818669	-6719.811237	0.7645	2.0290	-0.32
OH-bisNV ^{2(2+·)}	-12065.53164	-12065.52775	0.8911	2.0290	-0.19

The singlet-triplet energy gap (ΔE_{S-T}) was calculated according to the following equation proposed by Yamaguchi:^{S4}

$$\Delta E_{S-T} = \frac{2(E_S - E_T)}{\langle S^2 \rangle_T - \langle S^2 \rangle_S}$$

where the E_S and E_T is the total energy of the calculated broken-symmetry singlet state and triplet state, $\langle S^2 \rangle_T$ and $\langle S^2 \rangle_S$ is the total spin angular momentum of the calculated broken-symmetry triplet and singlet states.

The calculated results show that the ΔE_{S-T} of OH-bisNV^{2(2+·)} was larger than those of OH-bisMV^{2(+·)} and OH-bisOV^{2(+·)}, suggesting that the OH-bisNV^{2(2+·)} is more easily transformed from the singlet to the triplet state. It probably due to the electrostatic repulsion effect of positively charged quaternary ammonium groups at the terminal, and thus, weakening the pancake bond.

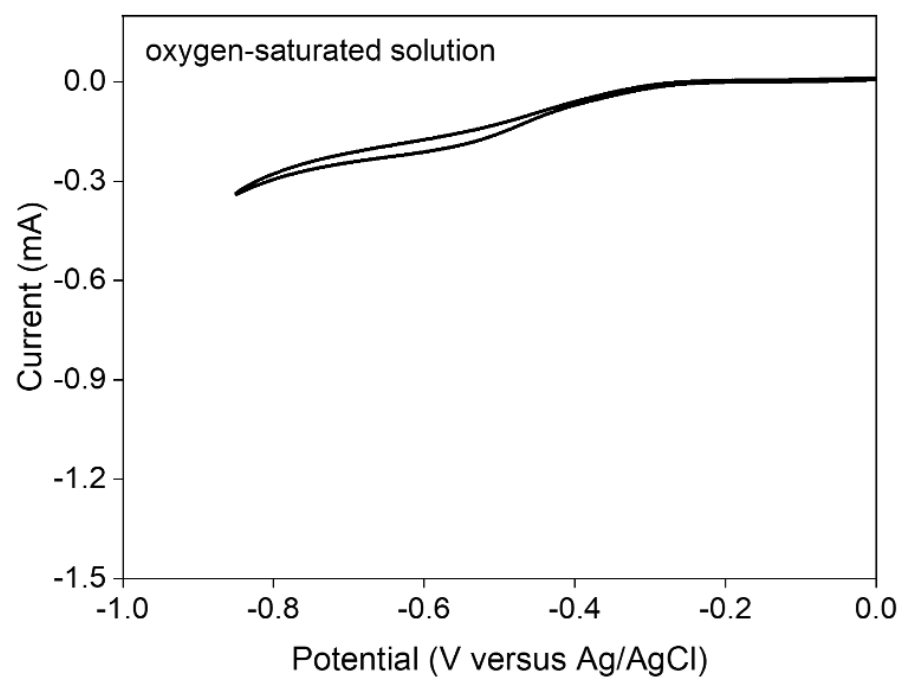


Figure S24. CV of oxygen-saturated solution recorded on the carbon paper electrode at a scan rate of 1 V s^{-1} (supporting electrolyte: 0.50 M KCl).

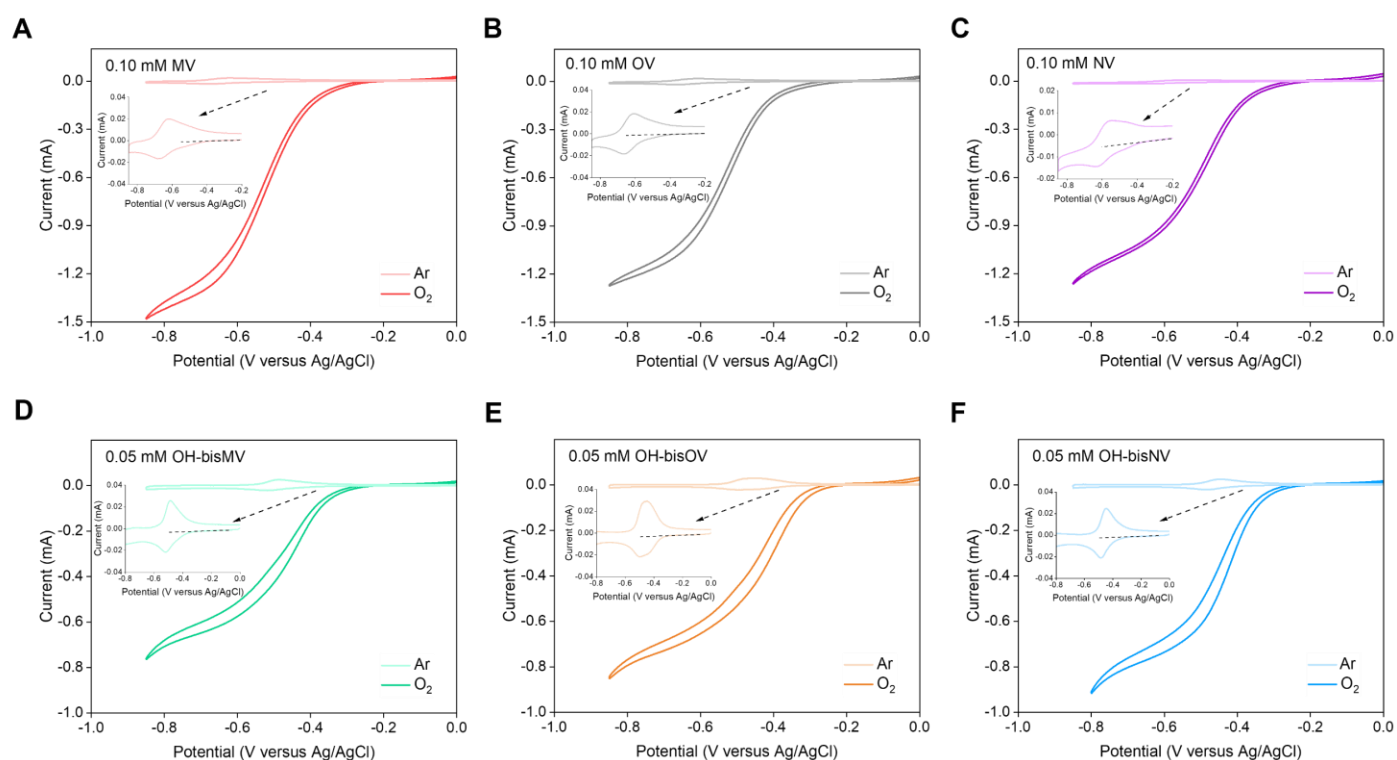


Figure S25. CVs of negolyte in Ar/O₂ atmosphere at a scan rate of 1 V s⁻¹ (supporting electrolyte: 0.50 M KCl). (A) 0.10 mM MV; (B) 0.10 mM OV; (C) 0.10 mM NV; (D) 0.05 mM OH-bisMV; (E) 0.05 mM OH-bisOV; (F) 0.05 mM OH-bisNV.

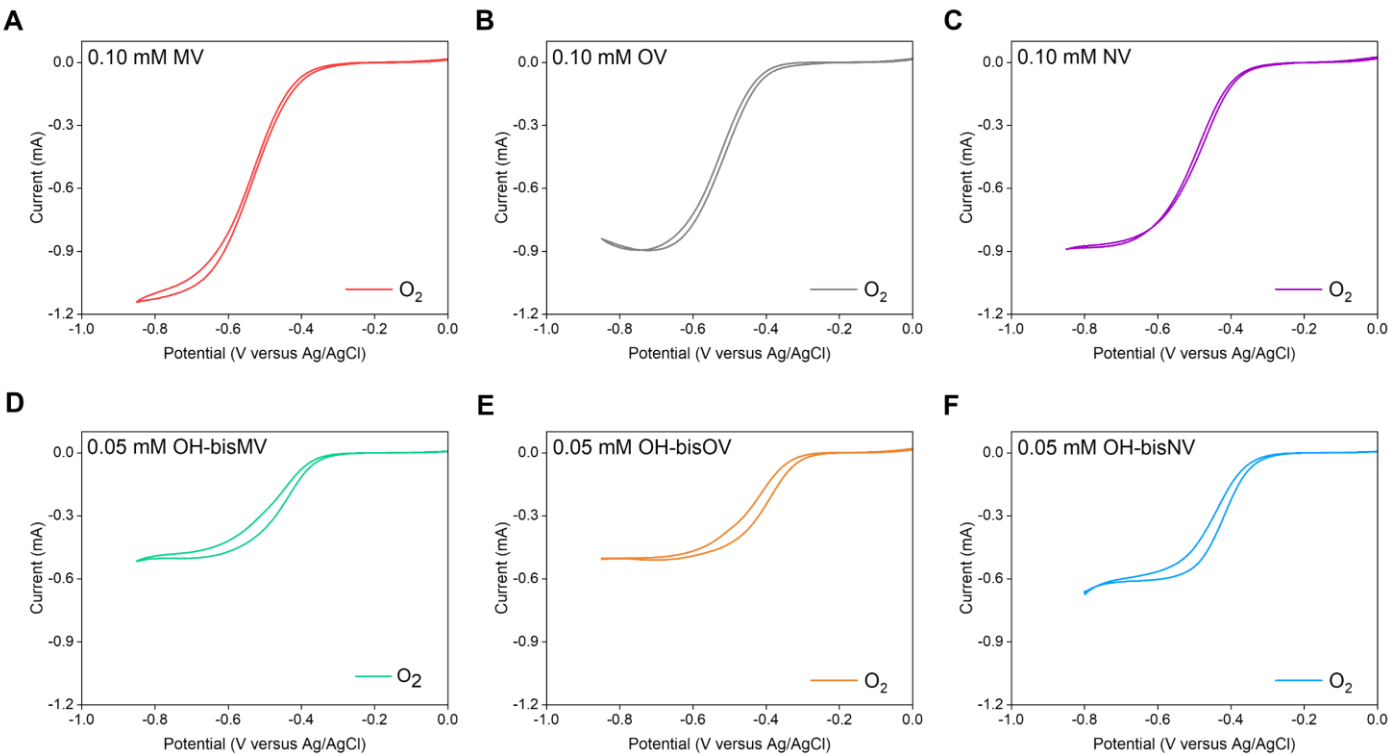


Figure S26. Background-subtracted CVs of negolyte in O_2 atmosphere at a scan rate of 1 V s^{-1} (supporting electrolyte: 0.50 M KCl). (A) 0.10 mM MV; (B) 0.10 mM OV; (C) 0.10 mM NV; (D) 0.05 mM OH-bisMV; (E) 0.05 mM OH-bisOV; (F) 0.05 mM OH-bisNV.

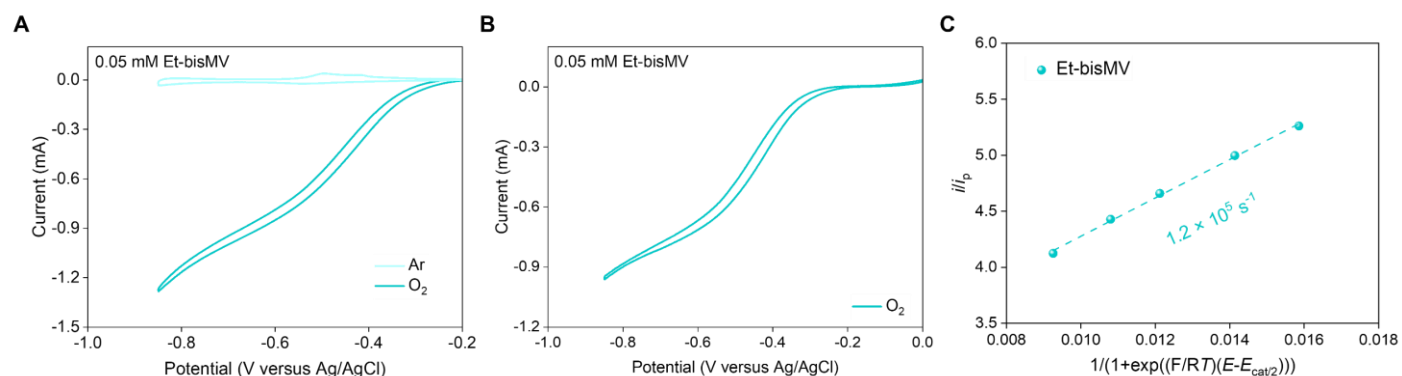
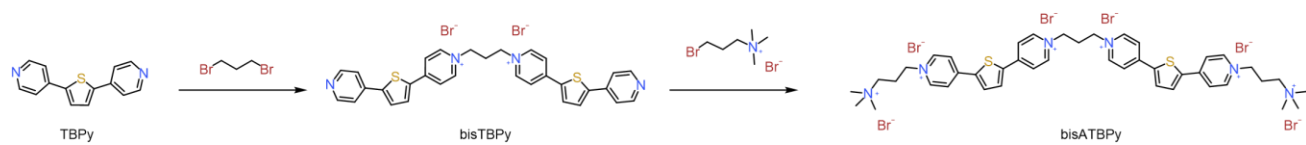


Figure S27. Determination of k_{obs} between O_2 and $\text{Et-bisMV}^{2(+)}$. (A) CVs of 0.05 mM Et-bisMV in either Ar or O_2 atmosphere (supporting electrolyte: 0.50 M KCl), scan rate: 1 V s^{-1} ; (B) Background-subtracted CV of 0.05 mM Et-bisMV in O_2 atmosphere; (C) The k_{obs} between O_2 and $\text{Et-bisMV}^{2(+)}$ derived from FOWA.



Scheme S5. Synthesis protocol of bisATBPY.

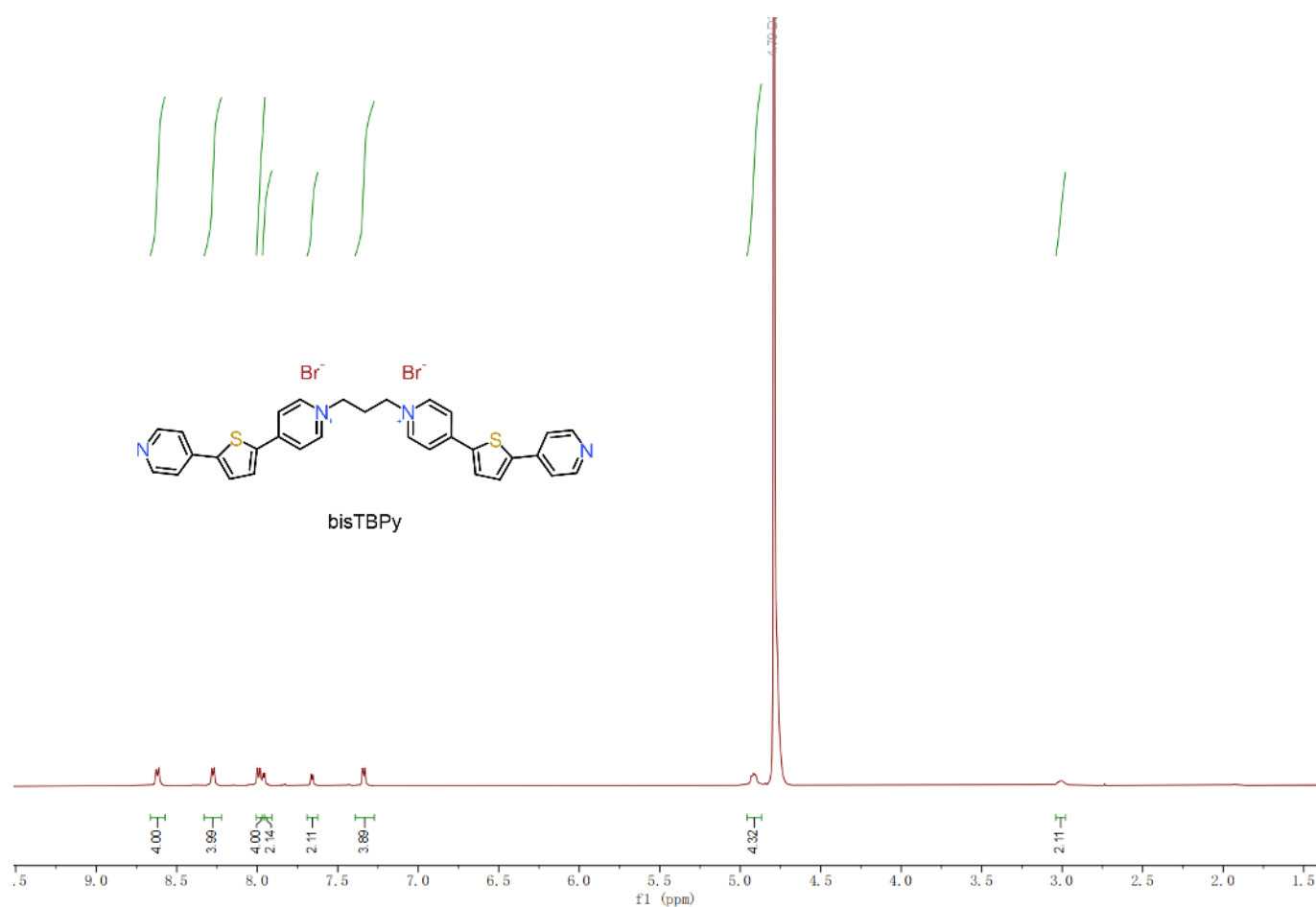
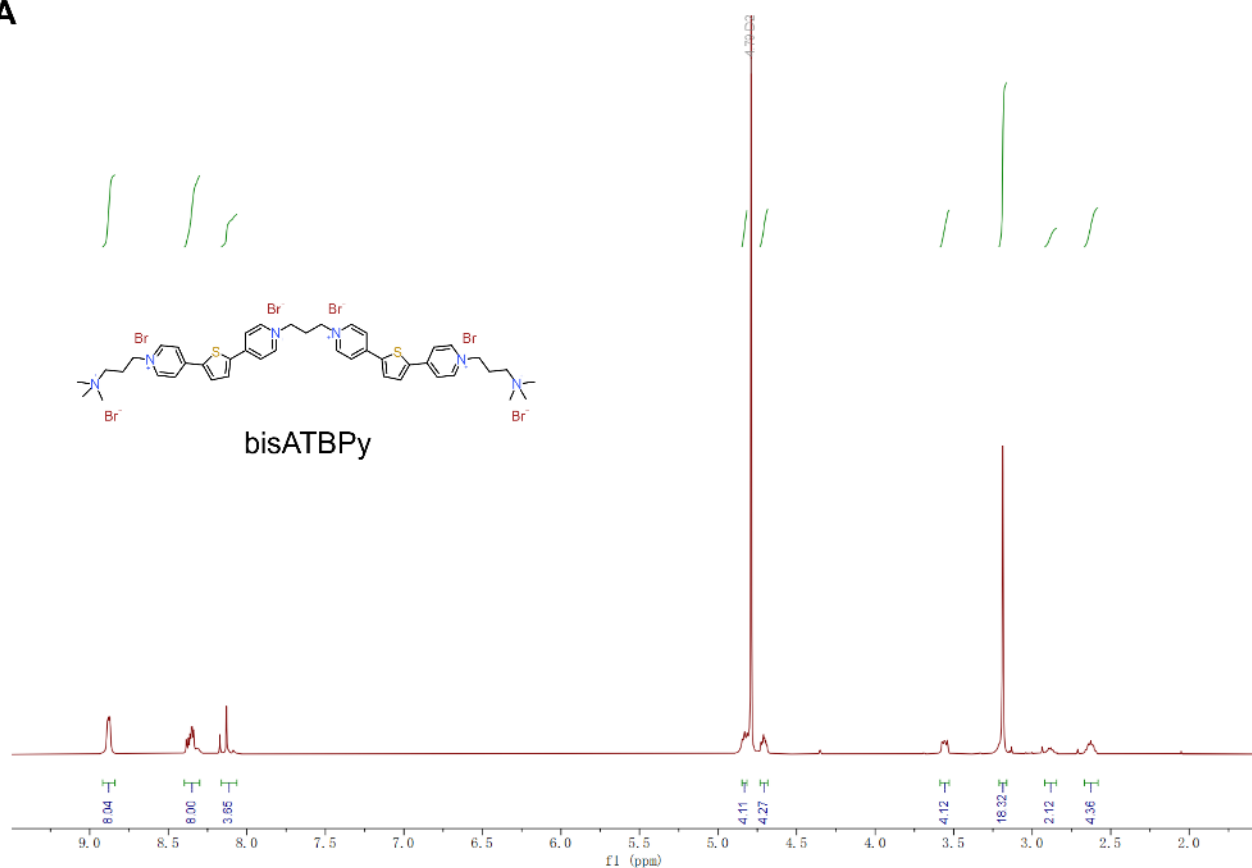


Figure S28. ^1H NMR spectrum of bisTBPY (D_2O).

A



B

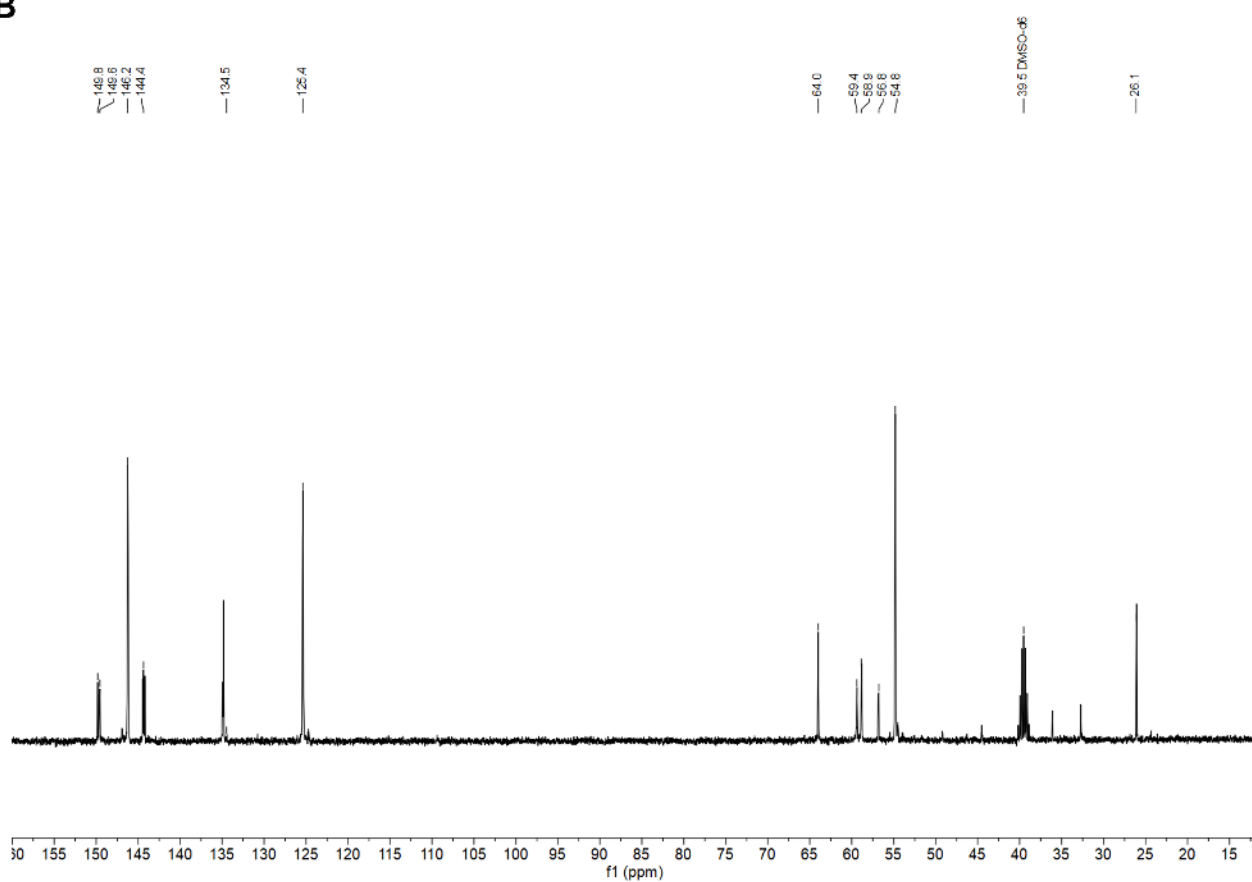


Figure S29. NMR spectra of bisATBPy. (A) ¹H NMR (D₂O); (B) ¹³C NMR (D₂O with a drop of DMSO-*d*₆).

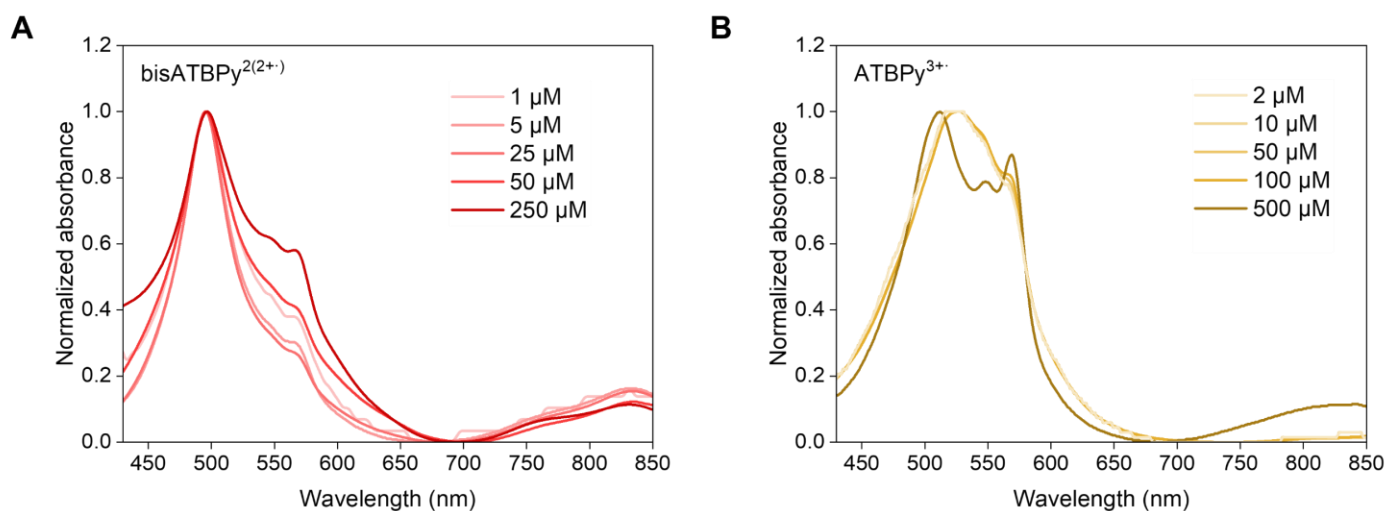


Figure S30. UV-vis-NIR spectra of negolyte at different concentrations. (A) bisATBPy^{2(2+·)}; (B) ATBPy³⁺.

To verify the intramolecular dimerization in the bisATBPy system, we conducted UV-vis-NIR spectroscopy measurements. As shown in Figure S30, the reduced-state bisATBPy^{2(2+·)} exhibits two characteristic absorption peaks at around 500 nm and 830 nm, respectively. The normalized curves at different concentrations (from 1 to 250 μM) almost overlap, indicating that the dimerization behavior of bisATBPy^{2(2+·)} is concentration-independent, namely, a typical intramolecular dimerization behavior. In contrast, the absorption band is not seen at 700 – 850 nm for monomeric ATBPy³⁺ when its concentration is below 100 μM. An absorption band emerges around 840 nm with an increase in concentration to 500 μM, suggesting a concentration-dependent intermolecular dimerization.

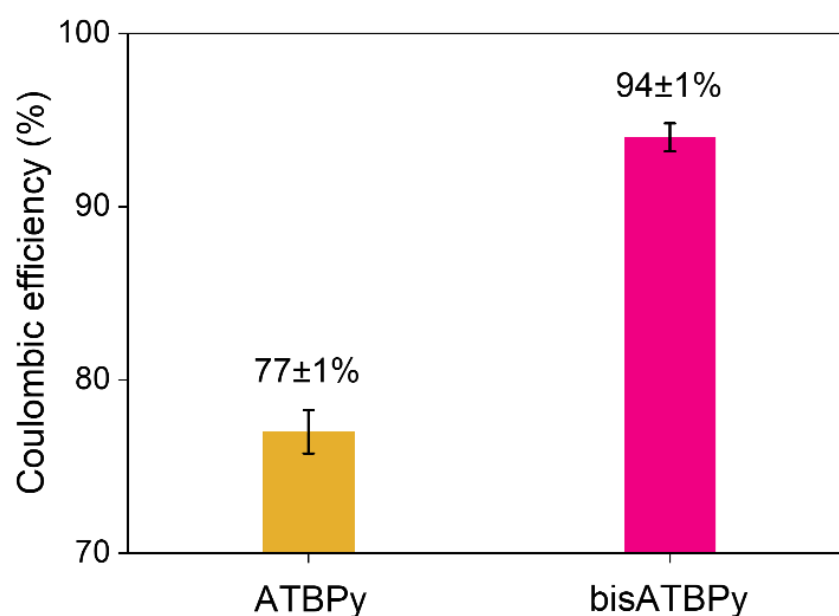


Figure S31. CEs of the flow battery ('open' system) under air with either 0.0125 M bisATBPy or 0.025 M ATBPy as the negolyte and 0.025 M FcNCl as the posolyte (Data are represented as mean $\pm$ SEM).

As shown in Figure S31, an 'open' system containing of bisATBPy negolyte shows a high coulombic efficiency of 94±1%, markedly outperforming the monomeric ATBPy^{S5} counterpart (only 77±1%) under identical conditions. These results demonstrate the generality of this strategy, suggesting its transferability to broader systems.

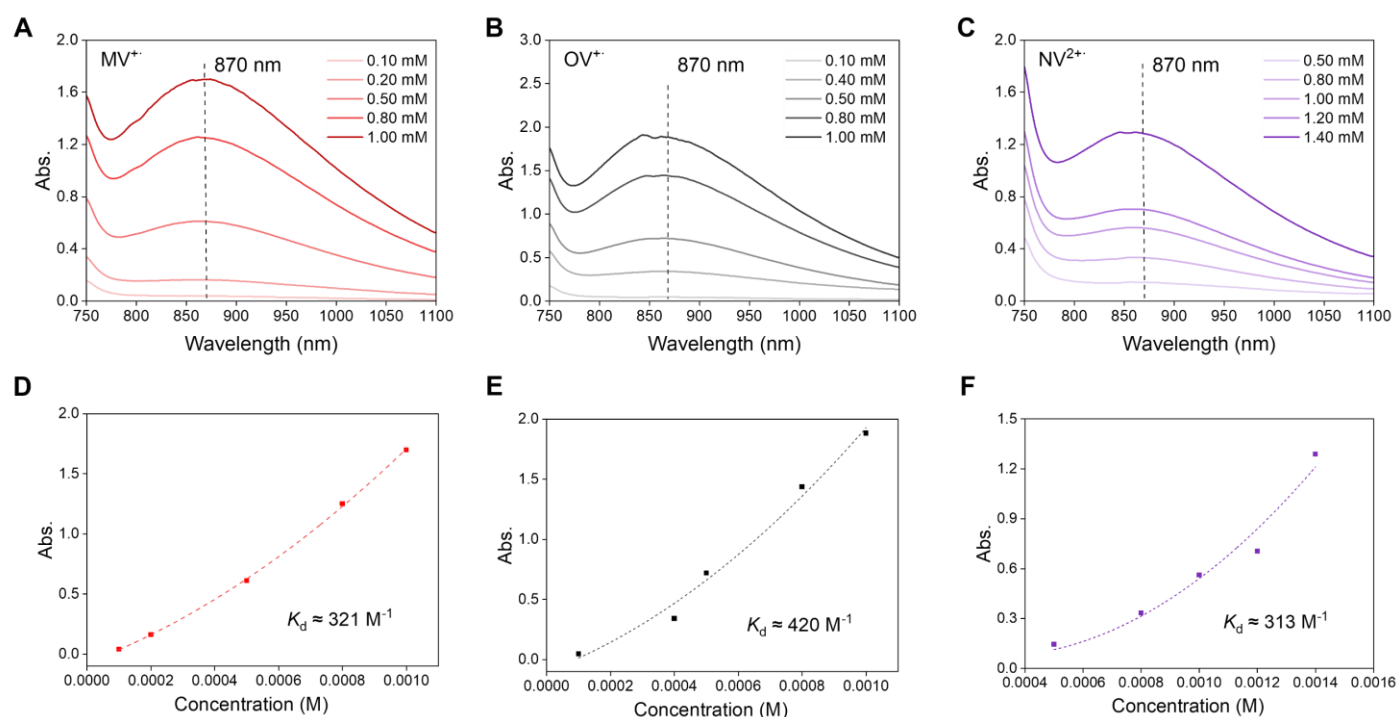


Figure S32. Determination of dimerization constant. (A) UV-vis-IR absorption spectra of MV⁺ at different concentrations; (B) UV-vis-IR absorption spectra of OV⁺ at different concentrations; (C) UV-vis-IR absorption spectra of NV²⁺ at different concentrations; (D) Dimer constant of MV⁺; (E) Dimer constant of OV⁺; (F) Dimer constant of NV²⁺. The dimer constant is obtained by fitting the absorption signal at 870 nm. The ϵ is taken as $2400 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. ^{S6}

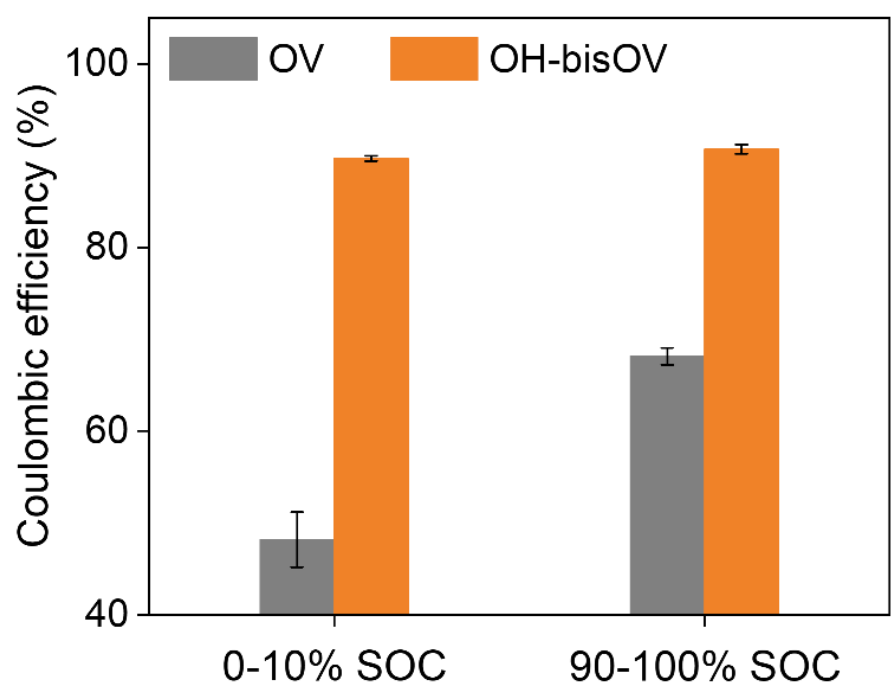


Figure S33. CEs of flow battery ('open' system) within different SOC intervals (0-10% SOC and 90-100% SOC) under air (Data are represented as mean $\pm$ SEM).

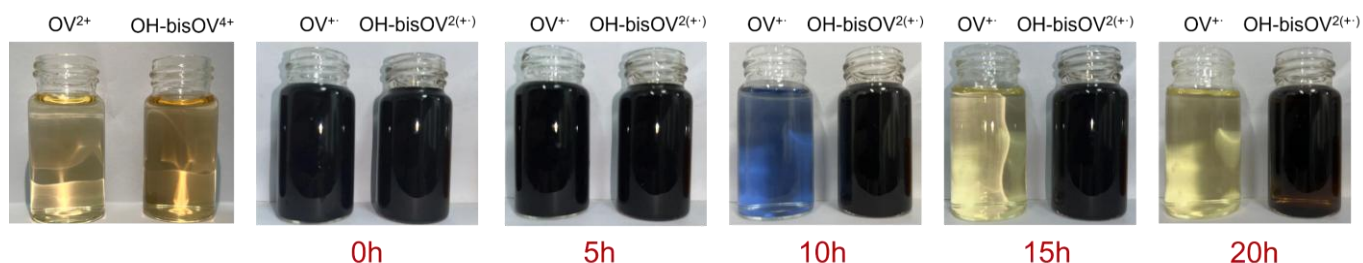


Figure S34. Photos of the 10.0 mL 10.0 mM OV²⁺ and 10.0 mL 5.0 mM OH-bisOV⁴⁺ electrolytes, and their reduced-state (OV⁺ and OH-bisOV²⁽⁺⁾) electrolytes exposed to air over different time.

The observed color changes lasting for several hours can be understood as follows. It is acknowledged that, the gas-liquid phase reaction can be described by the two-film theory.^{S7,S8} The overall reaction time is governed by the coupling of three processes (the transport of O₂, the diffusion of viologen radical, and the reaction in thin film).

① Process 1, the O₂ transport from the gas phase to the liquid film,

$$R_{\text{diff,o}} = \sqrt{k_r C_{v,l} D_o} A (C_o^{\text{eq}} - C_{o,l}) \quad \text{Equation S1}$$

where the $R_{\text{diff,o}}$ is the molar flux of O₂ (mol s⁻¹), k_r is the second-order reaction rate constant ($\sim 10^3 - 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$), $C_{v,l}$ is the concentration of viologen radical (Vi⁺) in the thin film (mol m⁻³), D_o is the diffusion coefficient of O₂ in the liquid phase ($2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), A is the interfacial area ($1.13 \times 10^{-4} \text{ m}^2$), C_o^{eq} is the equilibrium concentration of O₂ at the interface ($\sim 0.25 \text{ mol m}^{-3}$), and $C_{o,l}$ is the concentration of O₂ within the thin film (mol m⁻³).

② Process 2, the diffusion of the Vi⁺ from the bulk phase to the liquid film,

$$R_{\text{diff,v}} = D_v A (C_{v,b} - C_{v,l}) / \delta_{\text{eff}} \quad \text{Equation S2}$$

where the $R_{\text{diff,v}}$ is the molar flux of Vi⁺ (mol s⁻¹), D_v is the diffusion coefficient of Vi⁺ in the liquid phase ($\sim 6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), $C_{v,b}$ is the concentration of Vi⁺ in the bulk (10 mol m⁻³), and δ_{eff} is the thickness of the liquid film ($\sim 10^{-4} - 10^{-5} \text{ m}$)^{S9,S10}.

③ Process 3, the reaction within the thin film,

$$r = k_r C_{v,l} C_{o,l} \quad \text{Equation S3}$$

where r is the volumetric reaction rate (mol m⁻³ s⁻¹), governed by the bimolecular reaction between Vi⁺ and O₂ within the film.

Based on this model, the numerical solution by the SciPy tool shows that the reaction time in the reactor is 10 – 20 h as the 99% Vi⁺ molecules are oxidized by O₂. Such a timescale agrees well with the observed result (Figure S34). In addition, it is acknowledged that a slower reaction rate results in a lower $R_{\text{diff,o}}$ and higher δ_{eff} ^{S11}. Therefore, the color of the bis-viologen electrolyte can persist for a longer time than that of the mono-viologen.

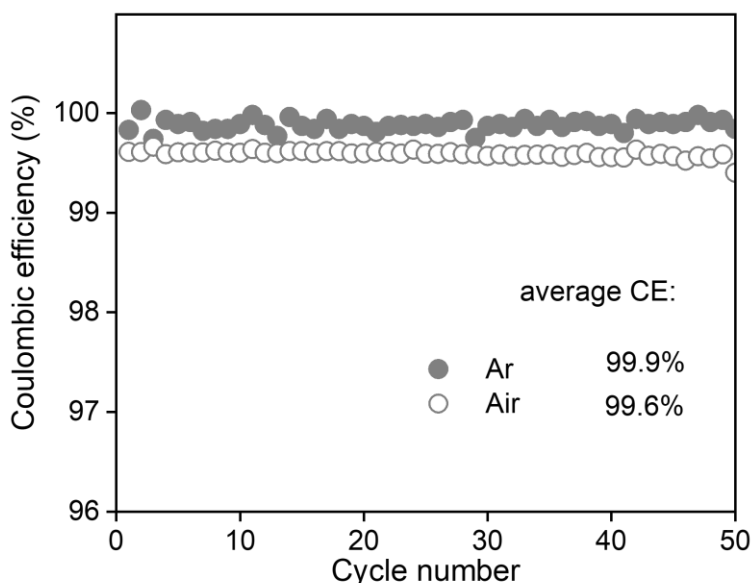


Figure S35. CEs of the flow battery fed with 0.50 M OV at 40 mA cm⁻² under air or Ar atmosphere.

The flow battery fed with 0.50 M OV electrolyte was operated under an Ar atmosphere. As shown in Figure S35, the average coulombic efficiency is about 99.9% under Ar, which is higher than that under air (99.6%). It is noted that the coulombic efficiency of OV-based flow battery under Ar is comparable to the OH-bisOV (Figure 4A). This result fully supports the conclusion that the low coulombic efficiency under air should attribute to the side reactions between residual oxygen and negolyte, rather than the intrinsic instability or the crossover of the molecule.

Precise quantification of the oxygen concentration in the reservoir is uneasy in practice. We, therefore, resort to roughly estimate it from the CE and cycle time of the OV-based flow battery. The numerical simulation based on the two-film model (*vide supra*), with all other parameters being held constant, indicates the oxygen fraction in the reservoir is ~100 ppmv, as inferred from the performance of the 0.50 M OV-based flow battery (CE ~99.6%, in Figure S35). At this oxygen level, the OH-bisOV^{2(+·)} negolyte would require ~1 h to undergo 0.1% conversion (corresponding to CE ~99.9%, in Figure 4A), far exceeding the cycle time of 20 min. As a result, the ‘closed’ OH-bisOV-based flow battery delivers a comparable coulombic efficiency and cyclability to that under Ar (Figure 4A).

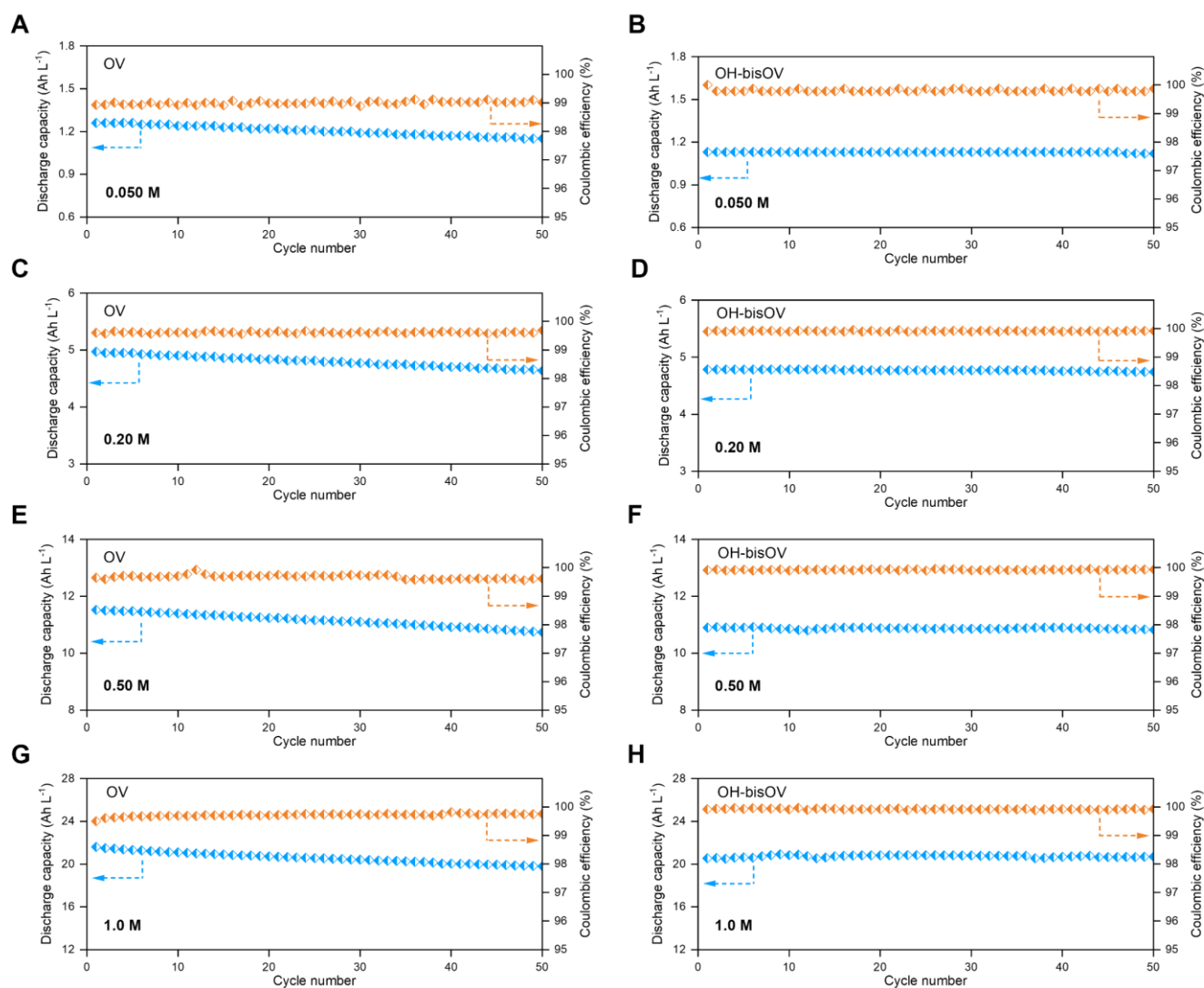


Figure S36. Cycling performances of flow battery ('closed' system) fed with different concentrations (electron concentration: 0.050, 0.20, 0.50 and 1.0 M) at 40 mA cm⁻² under air. (A) 0.050 M OV; (B) 0.025 M OH-bisOV; (C) 0.20 M OV; (D) 0.10 M OH-bisOV; (E) 0.50 M OV; (F) 0.25 M OH-bisOV; (G) 1.0 M OV; (H) 0.50 M OH-bisOV.

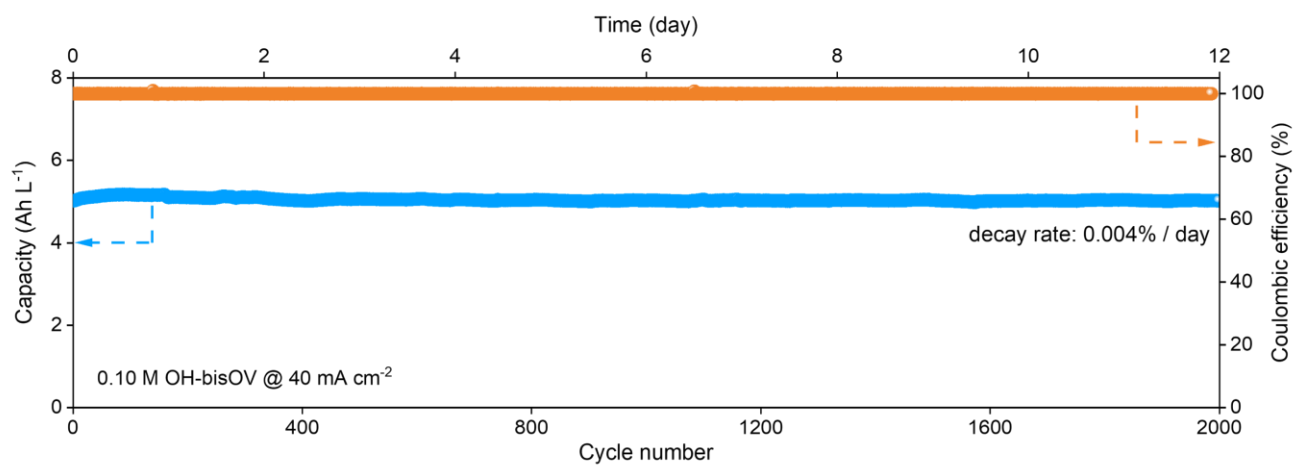


Figure S37. Cycling performance of symmetric battery fed with 0.10 M OH-bisOV.

Table S13. Summary of symmetric battery performances.

Negolyte	Concentration (mol L ⁻¹)	Capacity (Ah L ⁻¹)	Cycle time (day)	Decay rate (% day ⁻¹)	Ref.
OH-bisOV	0.10	5.02	11.9	0.004	This work
2,3-HCNQ	0.10	4.67	0.8	8.9	Wang et al. ^{S12}
2,6-DBEAQ	0.10	5.20	13.0	0.008	Kwabi et al. ^{S13}
2,6-DPPEAQ	0.10	5.30	6.0	0.02	Ji et al. ^{S14}
BPP-Vi	0.10	2.69	18.0	0.02	Jin et al. ^{S15}
R-Vi	0.10	N/A	7.6	0.47	Li et al. ^{S16}
S-Vi	0.10	N/A	7.6	0.82	Li et al. ^{S16}
2,6-D2PEAQ	0.10	5.07	2.5	0.07	Kerr et al. ^{S17}
2-QUIC	0.05	2.65	2.7	0.005	Modak et al. ^{S18}

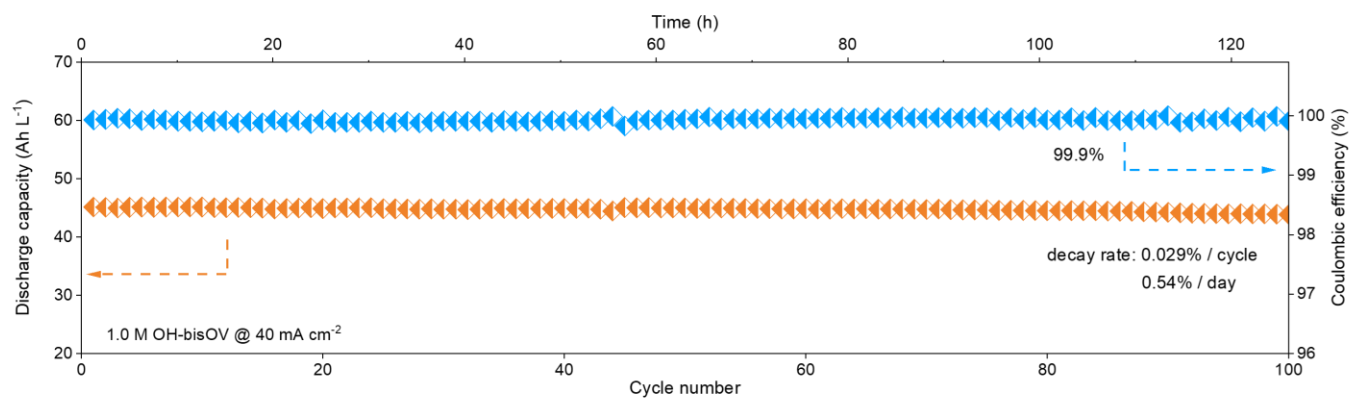


Figure S38. Cycling performance of the flow battery fed with 5.0 mL 1.0 M OH-bisOV and 100.0 mL 0.10 M FcNCl at 40 mA cm⁻² under air.

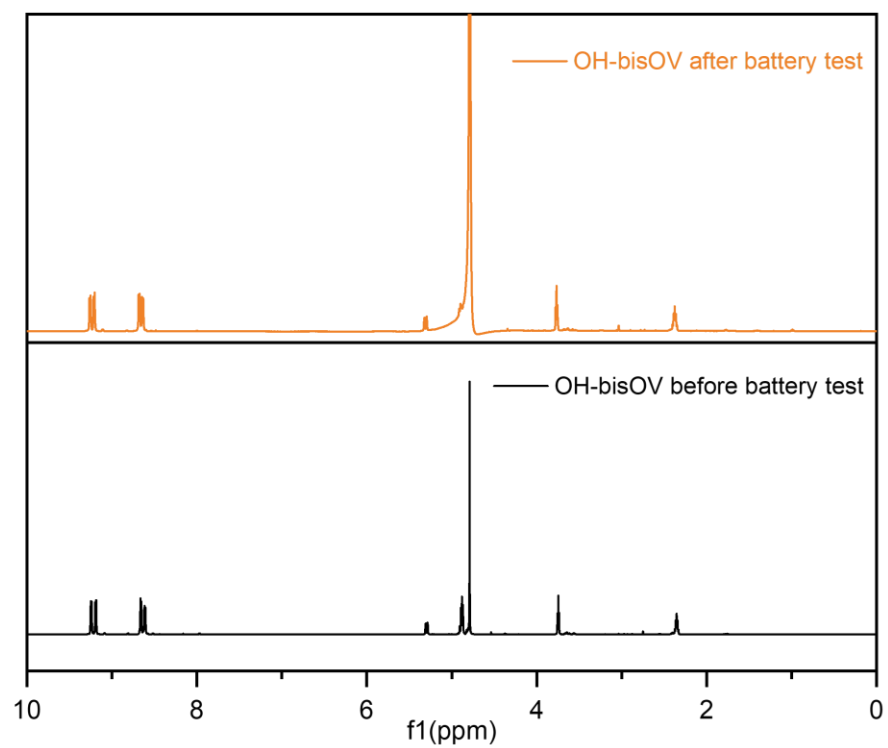


Figure S39. ^1H NMR spectra of OH-bisOV before and after battery test.

Table S14. Summary of full battery ('closed' system) performances under air.									
Negolyte	Capacity (Ah L ⁻¹)	Current density (mA cm ⁻²)	Cycle number	Decay rate (% cycle ⁻¹)	Cycle time (day)	Decay rate (% day ⁻¹)	Coulombic efficiency (%)	Atmosphere	Ref.
OH-bisOV	46.5	40	200	0.002	10.7	0.04	99.9	Air	This work
OV	21.6	40	50	0.17	1.2	6.94	99.7	Air	This work
BTMAP-Vi	13.65	40	50	0.7	~1.8	~16.4	99.5	Air	Beh et al. ^{S19}
(APBPy)Cl ₄	10.1	40	111	0.22	0.8	23.8	93.6	Air	Carrington et al. ^{S20}
(ATBPy)Cl ₄	8.0	30	100	0.36	3.3	9.08	97.9	Air	Carrington et al. ^{S20}
DBEP	4.4	50	400	0.03	~ 3.0	3.77	96.0	Air	Liu et al. ^{S21}
2-QUIC	5.3	20	60	0.015	1.25	0.70	98.0	Air	Modak et al. ^{S18}

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